METALLURGIA

THE BRITISH JOURNAL OF METALS

Vol. 48 No. 287 SEPTEMBER, 1953 Monthly: TWO SHILLINGS

30 SEP 1953

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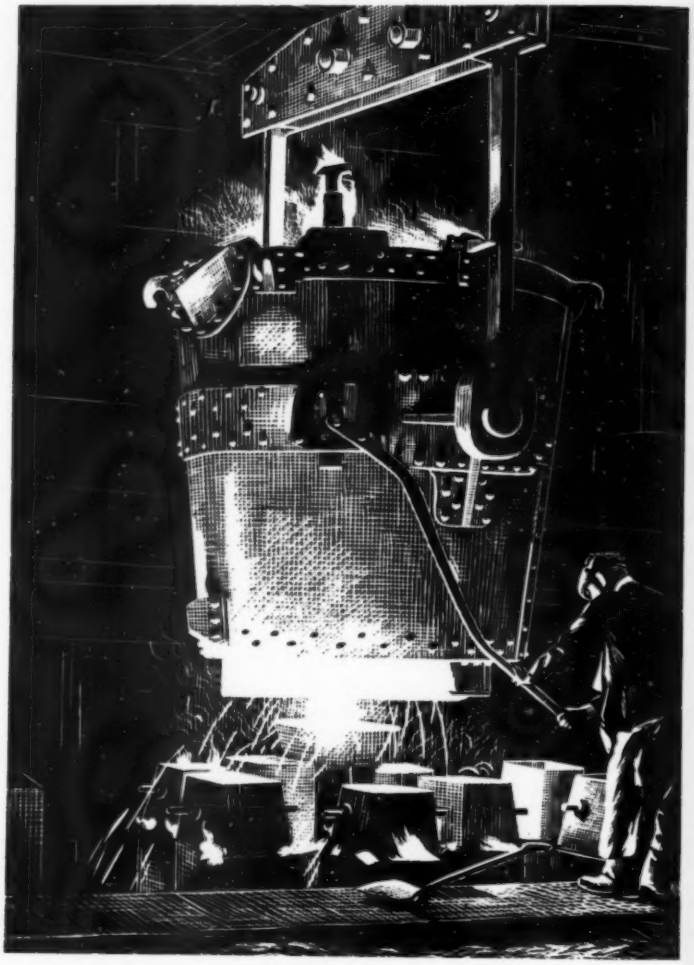

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INCORPORATING THE METALLURGICAL ENGINEER

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METALLURGIA

THE BRITISH JOURNAL OF METALS

INCORPORATING THE "METALLURGICAL ENGINEER"

SEPTEMBER, 1953 Vol. XLVIII. No. 287

Entry to Management

ANOTHER Trade Union Congress has come and gone, and many have been the resolutions debated—sometimes heatedly, sometimes more soberly—during its course. Perhaps the greatest general interest was raised by motions on nationalisation, wage restraints, and the Steel Board appointments. On the whole, the moderate elements won the day, but the voting was by no means overwhelmingly in their favour, and, in view of the not inconsiderable support which seems to exist for the extreme left wing of the Labour Party in the constituencies, it may be that it would have been even closer if the rank-and-file members of the unions had cast their votes individually, instead of by the block voting system. The extent to which extremist views have been accepted may, of course, owe much to the muddled thinking which has been evident on some of the major issues—particularly with regard to the Steel Board appointments. Although there may be genuine grounds on which trades unionists—depending on their outlook—could feel compelled to oppose the acceptance of such appointments, a good deal of opposition appears to have been generated by the erroneous belief that the Board was set up to denationalise the industry. Again, on the question of a wages policy, a union leader recently stated that he was not interested in productivity; all that interested him was the standard of living of the workers—as if the two things were completely divorced. It should be emphasised, however, that muddled thinking is not confined to the union side, nor is "wickedness" the monopoly of capitalists and employers.

Another kind of monopoly was concerned in a resolution moved by Mr. H. Knight (Association of Supervisory Staffs, Executives and Technicians): "This Congress, recognising the importance of raising the educational and technical standards of management in all levels of industry, calls on the General Council to investigate to what extent, and by what methods members of junior management are given opportunities of university training and graduates are being brought in from the universities, and to report to the next Congress on the problems that arise from these developments, with recommendations on the policy to be pursued." The General Council declined to accept the resolution, on the grounds that Congress had not the facilities for carrying out the type of investigation demanded, and on a show of hands the motion was defeated.

In spite of this defeat, the thoughts which prompted the resolution are worthy of consideration by industry as a whole. The fact is, of course, that many managerial positions are occupied—and successfully so—by university-trained men, but Mr. Knight said that after the report of the team which visited the United States to study management training under the auspices of the Anglo-American Council on Productivity, which stressed the higher proportion of graduates in managerial positions in America as compared with Great Britain: "some British managements," to quote *The Times* account of the proceedings, "were taking on young 'crackpots' from English universities and making them managers and supervisors after a year's experience of industry." It is a pity that the use of such terms should have been allowed to mar an argument which had its points on less histrionic but more logical grounds.

The fear underlying this resolution was that if this procedure were extended, skilled and knowledgeable craftsmen, who were capable of and deserving of higher posts, would never be able to enter the management, and the proposer denied the implication that the only men who could perform managerial functions satisfactorily were men from the universities, pointing out that a university training did not necessarily give that sense of human values essential to an understanding of the problems of human relationships in factories.

Few would defend the view that a university education followed by a year in industry is adequate training for management, but it is equally unsound to suggest that the fact that a man is a good craftsman, conscientious, and diligent, automatically makes him suitable for promotion to supervisory work. A university education, provided it has been on the right lines and has taught him to think, to appreciate all aspects of a problem, and to reach a sound decision on the available facts, should be of immense value to a man in his attempt to reach the top, but it is not a key to the board room in itself. In supporting the motion, Mr. J. H. Williams (A.S.S.E.T.) pointed out that American university graduates started on the shop floor, not two-thirds way up the ladder, but it must be realised that there is a very different attitude on the part of American trade unions towards workers who have not served a recognised apprenticeship. Furthermore, there is no necessity for a man to be a highly skilled operative in order to occupy a managerial position in a firm employing highly skilled operatives. True, he must have sufficient knowledge of the operations involved to appreciate their possibilities and limitations, but if he spends too much time acquiring manual skill he will have to neglect more important things.

Although a university training should give a man a good basis on which to build experience that will eventually fit him for management, not all graduates will make good managers—no matter how brilliant they may be academically. On the other hand, some, at least, of those employed on the shop floor will have the ability to serve in a higher capacity, and it seems essential that any system of appointments should be sufficiently flexible to allow the promotion of whoever may be most suitable for the vacant position. Much has been said and written about incentives, but perhaps the greatest incentive of all is the knowledge that it is possible to improve ones position—in spite of the cynic's advice: "If you work hard eight hours a day and don't worry, you may one day become the boss, work sixteen hours a day, and have all the worry."

More Turkish Copper

TURKEY has, in the last five years, developed a major producer of strategically vital copper in the Murgal mine, in the north-eastern corner of the country. From its smelter near Hopa, the Murgal mine is producing now at the annual rate of 12,000 tons of copper, and within a year, the production is expected to be increased to 15,000 tons.

Development of Murgal's facilities began under the Marshall Plan in 1948 and technical experts of the Mutual Security Agency who went to Hopa in 1952 to spur copper output for defence needs found what they described as equipment equalling any in use in the world. The state-owned Etibank, which controls Murgal as well as all other Turkish mining enterprises, had invested the equivalent of nearly $10 million in the mine and plant since the war. This was part of a broad post-war investment programme for mining coal, chrome, copper and manganese totalling nearly 370 million Turkish lira, (about $132 million) and financed in very large part by American aid supplied by the Marshall Plan and the Mutual Security Agency. In addition to yielding a strategically important product, Murgal has become a major earner of foreign currency for Turkey.

Two Mutual Security Agency mining and refining specialists arrived at Murgal in March, 1952, together with two American foremen to supervise plant operations. They demonstrated that the plant's productivity could be substantially increased through relatively minor changes in operating procedures. Immediately on arrival they went to work with the Turkish plant engineers to make adjustments to the reverberatory furnace, adjustments which resulted in the smelting of higher tonnages with lower coal consumption. Under their guidance, Turkish workers in the plant shops built spray guns for patching, to keep the furnaces in full and constant operation. Ore is brought 2·5 km. from the mine shaft to the smelter by an aerial trolley, which now operates 16 hours per day. Present output of the smelter is 35 tons of blister copper daily, but changes now under way will increase daily output to 40 tons within the next year. To effect this increase, the aerial trolley will be put on 24-hour working schedule, manned by three 8-hour shifts. At present the total work force in the mine and smelter totals 1,800 men.

The copper content of the Murgal ore averages 4½ to 5%, though some of the ore contains as high as 8% copper. A flotation process operated by pressure from a 106 m. high water tower converts it into ore washed, ground, freed from gases and other foreign elements and with a purity between 25 and 30%. High pressure pipe moves it on to the filtration process, where it becomes a paste which, after drying, is ready for the blast furnace.

Reserves of copper at Murgal are estimated to be about 13·5 million tons, and exploratory drilling is still being carried on by the Etibank. As part of the continuing development of its own property the Etibank has announced plans for starting the production of sulphuric acid and superphosphate as smelter by-products. Sulphuric acid production, which will be undertaken at Murgal, will be of importance to Turkey's industrial development. The superphosphate plant, to fill a constantly growing demand for fertilizer in Turkey, will be set up at Trabzon, further west along the Black Sea coast.

Portable Aluminum Test Masts

THE system of wireless transmission at "very high" and "super high" frequencies is now being used on an increasing scale for television and telephone links. As the short waves are effectively interrupted by physical obstacles such as hills, or the curvature of the earth, the system requires a series of receiving and retransmitting stations within "visual" range of each other, and hence at relatively frequent intervals along the line of transmission.

Establishment of a new line has to be preceded by tests to discover the best site for each relay station and the height of mast that will be needed, and for this work pairs of temporary test masts, carrying transmitting and receiving equipment, are employed. Structurally, these test masts must be easily transportable to the sites over all types of country and capable of being quickly erected and dismantled by a small crew. A further essential is that the height of the directional transmitting and receiving aerials and reflectors on the masts should be readily adjustable. A pair of 200 ft.-high test masts to meet these requirements has recently been built for Standard Telecommunication Laboratories, Ltd., by Painter Brothers, Ltd., Hereford, to the design of British Insulated Callender's Construction Company, Ltd.

Each mast is of lattice construction, triangular in cross-section, and is built up from a number of short, easily-handled lengths: it is guyed at several points. The material chosen for the structure was the aluminium alloy, Noral 51SWP, supplied by Northern Aluminium Co., Ltd. This alloy, which meets B.S.1476 HE10, is of the aluminium-silicon-magnesium type now widely used for structural work, having a typical tensile proof stress of 18 tons/sq. in., and sufficient durability to enable it generally to be used without painting. Each length of mast, 8 ft. 4 in. long, weighs only 110 lb., and is easily handled by two men aloft with the aid of a light-alloy erection pole.

Bolted construction was chosen for the mast, so as to enable the individual lengths to be further broken down to any degree necessary for shipment over long distances, for instance by sea. In general, the bolts are of Noral 51SWP alloy like the members, but high-tensile steel is used for the bolts that connect each length to the next. Mild steel is used for various details at the butt joints and at guying points. All steel parts are galvanised to prevent atmospheric corrosion and to avoid any possibility of galvanic interaction with the aluminium. A special section was designed for the main leg members, which assist in guiding the test equipment up and down the mast. The readiness with which complex, multi-purpose sections can be produced by extrusion is, of course, one of the advantages of aluminium as a structural material.

One 200 ft. mast, complete with steel head and base plates, wire ropes and fittings but excluding anchorage pickets, weighs just over 1¼ tons. With all materials on site and the pickets driven in, the whole structure can be erected by six men in an eight-hour day; where the full height is not required, erection time is reduced. The first two masts have proved themselves satisfactory in service and a further six are being built, though development work is still proceeding and may show the possibility of further improvement.

Hot Dip Aluminising

By M. L. Hughes, Ph.D., M.Sc., F.R.I.C., F.I.M.
and D. P. Moses, B.Sc., A.I.M.
British Iron and Steel Research Association South Wales Laboratories.

After reviewing the published information on the hot dip aluminising process and on the properties of the product, the authors describe work carried out on the subject in the laboratories of The British Iron & Steel Research Association at Swansea, as a result of which the preliminary treatment of the strip prior to aluminising has been greatly simplified. The effect on the product of variations in the aluminising process has been examined, including their influence on the properties of the steel base. Experimental batch aluminising procedures and the operation of a pilot plant for continuous coating are described. Finally, the advantages and disadvantages of the process and its product are discussed.

THE value of aluminium as a protective coating on steel is now generally recognised, largely due to the good results obtained in recent years with sprayed aluminium coatings, but work done on hot dipped aluminium coatings has shown that this type also has valuable properties. Tests carried out since 1932/33 by the American Society for Testing Materials have shown that a hot dipped aluminium coating gives, in most cases, better protection than a zinc coating of equal thickness and, therefore, more than twice the weight. This superiority is more pronounced under humid or sulphurous conditions, when zinc coatings are liable to fail rapidly. In recent years cold-reduced wide strip has been successfully hot dip aluminised in continuous units, and the product (Armco-Aluminised sheet) is being increasingly used for its resistance to heat and corrosion.

The application of the coating by hot dipping has proved to be a difficult process in some respects. The earlier attempts to overcome the difficulties were reviewed by E. J. Groom in 1937[1]. A variety of fluxes, usually based on alkali chloride with the addition of cryolite, have been tried, and thin coatings of tin, zinc, nickel, cadmium, and possibly other metals, have been used to protect the steel surface immediately prior to immersion. Brushing during immersion was also recommended, followed, if necessary, by re-dipping.

The use of reducing gases in the preliminary treatment of the wire or strip, and also as a protective atmosphere in an enclosed dipping chamber, had been patented at this time. Fink's process[2] is an example of the former type which required the heating to a high temperature of the cleaned sheet, strip or wire in hydrogen; sufficient hydrogen was said to be absorbed to facilitate the coating process. A protective atmosphere was also employed on the emergent side, and wire was said to be coated by this method at ten to fifty feet per minute. A protective atmosphere over the bath itself was used by Dellgren in several types of process: in one[3], the articles were immersed in flux before dipping, and in another[4], strip was passed through a lead bath and then upwards through molten aluminium floating on the lead at the exit end. Some of these early processes were said to require very high temperatures (e.g. 900° C.) and long times of immersion (e.g. 2 minutes) before a satisfactory coating could be obtained.

The addition of alloying elements to the molten aluminium has been suggested. Dellgren[5] and Nillson[6] proposed to use zinc, and the addition of silicon, in small quantities, was patented[7]. H. Röhrig[8] examined the influence of silicon on the alloying action between iron and aluminium, and found that an addition of 5% silicon to the bath halved the thickness of the alloy layer formed. The addition of silicon is an essential feature of the modern aluminising process, and the progressive change in the coating structure with increasing silicon has been described by Stroup and Purdy[10]. The influence of a wide range of elements when added to an aluminising bath was examined by Gittings, Rowland and Mack[11], who found that only beryllium and copper were comparable with silicon in their effects. Beryllium is much more powerful than silicon, but is expensive and requires care in handling because of its toxic properties.

The Armco and Alferieff Aluminising Processes

More recent developments have been chiefly towards perfecting the method of preheating the sheet or strip in a reducing atmosphere, so as to produce a surface ready for immersion in the molten bath without the use of a molten flux. In America, Sendzimir hot galvanising units have been adapted by Armco for hot dip aluminising cold-reduced steel strip, and over a period of more than ten years the product has been found to have many applications. It has been stated that in 1950 hot dip aluminising in the U.S.A. consumed 1,000 tons of aluminium, and this figure has probably been greatly exceeded since that date. In the Sendzimir process[9], the cold-reduced strip is first lightly oxidised to a temper colour, then annealed in a protective atmosphere of cracked ammonia and allowed to remain in that atmosphere right up to the point of immersion in the molten bath. Pickling and fluxing, with their attendant troubles, are eliminated. This method of preparation has contributed greatly to the successful production of Armco-Aluminised sheet. The addition to the bath of silicon, beryllium, cerium, and possibly other elements such as magnesium, has improved the ductility and appearance of the product, and this is discussed later.

A process for the continuous aluminising of strip steel has also been patented by Alferieff[12] and was described in 1942[13]. A further account by Alferieff of this process appeared in 1945[14], and an extended abstract of this paper has been prepared by Dr. J. C. Hudson[15] from the original French. A description of the Alferieff process has also been given by Guillet[16] and an English version

of this is available as Henry Brutcher Translation No. 2496. The process resembles the Sendzimir process in many respects, but differs in that water vapour is introduced into the high temperature zone in order to effect some decarburisation of the steel surface. The bath is aluminium of 99·5% purity, i.e., normal commercial quality, and is thus not heavily alloyed with silicon as in the Armco aluminising process. The process depends upon a short time of immersion and a minimum operating temperature for preventing excessive alloy growth in the absence of silicon. Output is said (by Guillet) to be 8 tons of strip in 24 hours, but Alferieff refers to 6,000 tons a year. The physical properties of the coating are said to be good, though it is liable to crack under compression. The coating applied is equivalent to 0·6 mils thickness and reference is made to a subsequent re-rolling for surface finish.

Other Aluminising Processes

Methods of hot dip aluminising based on the use of fluxes are still being examined, but there is little indication of much commercial progress. A recent modification is to float the molten aluminium on a molten salt bath of suitable density which acts as a flux. The necessary density is obtained by using barium chloride, and the fluxing properties by the use of alkali chlorides and cryolite. In the Möller process[17,18], the steel is lowered through the aluminium into the flux and then raised through the aluminium layer again. It is also possible to use the layer of salt at the bottom as an electrical resistance ; electrodes are immersed in the bath and the temperature of the floating aluminium can be closely controlled. This simplifies the problem of the container, which may now be lined with refractory material in order to reduce iron pick-up. This advantage may also be achieved by induction heating.

Although, in recent years, attention has been devoted mainly to the continuous aluminising of strip, the aluminising of fabricated articles by a batch process has also been studied. Fink[19] claims the successful coating with aluminium of stampings, forgings, and even castings. The essence of his process appears to be the blowing of hydrogen into the molten bath, an atmosphere of hydrogen being maintained above. He states that " no special pre-treatment of the basis metal is required."

The hot dip aluminising of cast iron articles has been described by Whitfield and Sheshunoff[20], who give some details of the resistance of aluminised steel and cast iron to high temperature in the presence of sulphurous gases. These materials are said to be much superior in this respect to stainless and heat resisting steel. In the case of cast iron, the coating prevents oxidation and reduces " growth." The time of immersion is said to be " a few minutes " and the temperature not critical. A coating thickness of 5 mils is quoted. A production process for the aluminising of heat exchanger units has been described[21] in some detail. It consists of the usual cleaning processes, degreasing and pickling, followed by preheating and fluxing in molten flux contained in an electrically heated furnace. Dipping is carried out in a second furnace, heated by induction, containing pure aluminium with a floating cover of flux. The time of immersion here is 30 seconds to 1 minute, and excess aluminium is removed by an air blast.

The various patents and descriptions of processes include some obvious contradictions. In one case[2] it is considered important to saturate the steel with hydrogen, and in another[19] to saturate the bath by pumping in hydrogen—both ideas being due to Fink. On the other hand, Alferieff is insistent that the steel must not be allowed to absorb hydrogen, either from the protective atmosphere or as a result of the treatment with steam at high temperature. He stipulates a vigorous purging of the final section of his furnace with an inert atmosphere free from hydrogen. Information concerning the preliminary treatment of the steel is also contradictory, the preparation being complex in some cases but simple in others. Recommendations concerning the dipping temperature vary, and some high temperatures are mentioned.

Although the use of a molten salt bath for fluxing and preheating fabricated articles has meant, according to one source[21], that " complex parts are easily coated with aluminium," it has also been stated[22] that " the use of a liquid flux adds to the difficulties," and that " the use of flux coverings on the bath is also unsatisfactory." The remedy lies, it is stated, in adjusting the composition of the bath. In addition to the use of silicon to reduce and modify the alloy layer, small amounts of lithium, beryllium and cerium (as *mischmetall*) are said to effect some improvement by reducing surface roughness and staining.

Corrosion Resistance of Aluminium Coatings

Aluminium coatings on steel would be expected, from the relative electrochemical characters of iron and aluminium, to be anodic to the basis material, and to afford " sacrificial " protection under conditions leading to wet corrosion. It is found in practice that the electrochemical behaviour of the coating depends to a large extent upon the environment. This is due to the presence of a resistant film of oxide which, in most cases, makes the coating cathodic to the steel base. When the exposure conditions are such that the oxide film is broken down, the coating is found to be anodic.

The atmospheric exposure tests carried out by the A.S.T.M. Committee A5 (Corrosion of Iron and Steel), Sub-Committee VIII (Field Tests of Metallic Coatings), have demonstrated the value of hot dip aluminised coatings. Samples of hardware of various kinds, structural shapes, tubes, window-sections, etc., were exposed at five stations. It was obvious, as long ago as 1944[23], that the aluminium coatings were giving remarkably good results, in most cases superior to those given by hot galvanised coatings even when the latter were thicker and, therefore, more heavier. For example, after 10·3 years exposure to the corrosive atmosphere of Pittsburg, " all specimens had rusted completely except those coated with aluminium, those coated with lead, and some of those coated with zinc. Rusting had started on all zinc and lead coated pieces. The aluminium coatings were dark but free from rust." The specimens referred to in this report include those detailed in Table I, and the respective coating weights should be noted. When the coating values are converted to thicknesses, in all cases except one (No. 10), the aluminium value is lower. (Samples of hardware in cast iron and malleable iron included in this test had much heavier aluminium coatings).

Similar samples exposed at four other stations also showed that hot dipped aluminium coatings were as good as, or better than, hot galvanised coatings which were in many cases much heavier. Reports after 12·8 years at these stations closely resembled that quoted above.

TABLE I.—SAMPLES OF GALVANISED AND ALUMINISED STEEL EXPOSED AT BRUNOT ISLAND, PA.

Sample	Base	Coating Weight (ozs./sq. ft. surface)	
		Hot Dip Galvanised	Hot Dip Aluminised
1. 3" × 3" × $\frac{1}{4}$" Steel Angles ..	Plain Carbon Steel	2·52	0·89
2. 3" × 3" × $\frac{1}{4}$" Steel Angles ..	Copper Steel	2·88	0·82
3. 3" × 1$\frac{1}{2}$" × $\frac{1}{4}$" Steel Angles ..	Plain Carbon Steel	3·24	0·75
4. 3" × 3" × $\frac{1}{4}$" Steel Angles ..	Copper Steel	2·75	0·50
5. 1$\frac{1}{2}$" × 1$\frac{1}{2}$" × $\frac{1}{4}$" Steel Angles ..	Plain Carbon Steel	3·16	0·89
6. 1$\frac{1}{2}$" × 1$\frac{1}{2}$" × $\frac{1}{4}$" Steel Angles ..	Copper Steel	3·20	1·11
7. $\frac{1}{4}$" × 3" × $\frac{1}{4}$" Steel Angles ..	Plain Carbon Steel	2·49	0·90
8. $\frac{1}{4}$" × 3" × $\frac{1}{4}$" Steel Angles ..	Copper Steel	2·67	0·66
9. No. 209 Window Frame Sections	—	3·10	0·61
10. No. 192 Window Frame Sections	—	2·60	1·39
11. No. 161 Window Frame Sections	—	2·97	0·66

It was observed during this work that corrosion occurred at threads which had been re-cut after aluminising. This is an example of the lack of electrochemical protection liable to occur with aluminium coatings. It was also noticeable that the superiority of the aluminium coatings was less marked in marine locations.

The coating on Armco-Aluminised sheet is much thinner than those given in Table I. A panel, 8 in. × 9$\frac{1}{2}$ in. × 20 s.w.g. (0·036 in.), supplied by the makers and examined in 1951, was found to be very uniformly coated to a thickness of 0·8 mils, equivalent to 0·20 oz./sq. ft. of surface. Samples received in 1944 and examined by the Corrosion Committee of the Iron and Steel Institute (Atmospheric Corrosion Sub-Committee) were more thickly coated, some having from 1 to 1·5 mils, but one sample having 2·5 to 3 mils. Corrosion tests on these samples were carried out in several laboratories and reported in 1946[24]. Failure to protect at cut edges was observed, but the resistance of the coating was otherwise satisfactory. After eleven months exposure to intermittent salt spray testing, it was concluded that "the protection .... by the aluminium coating was very good." Atmospheric exposure at Sheffield also gave satisfactory results. The rate of attack was said to be greater than on pure aluminium samples, and the aluminised coating was said to be inferior to a sprayed coating of aluminium, 3 mils thick. Later reports on these samples included a reference to the localised pitting which is likely to occur at exposed areas when the coating fails to provide electrochemical protection[25]. An examination of the behaviour of this material in various waters[26] showed marked differences with different waters, and also on heating the water.

These results did not appear to support the claim made by the makers that Armco-Aluminised steel had "a coating life ... six times that of zinc coatings of equal weight." On the other hand, Finkbone[27] refers to tests which showed that, after four years exposure in a mild industrial atmosphere, hot dipped aluminium coatings lost approximately one tenth as much weight as galvanised coatings under the same conditions. Samples exposed for two years in a marine atmosphere lost about one fifth as much weight as galvanised coatings. Galvanic protection at cut edges was found to be less than with zinc coatings.

Sprayed aluminium coatings have shown excellent resistance to atmospheric corrosion. The good results obtained industrially have been confirmed by exposure tests carried out by Hudson[28]. These coatings were thicker than the hot dipped coatings discussed here—more than 3 mils as compared with about 1 mil. The porosity and lack of ductility of a sprayed aluminium coating make it unsuitable for application to sheet where deformation occurs, but its good corrosion resistance suggests that the thinner hot dipped coating should have a satisfactory life. Hot dip aluminised panels exposed by Hudson gave results much inferior to those of the sprayed samples, despite a surprisingly thick coating applied to them. The bath was, presumably, pure aluminium, and the thick coating was probably the result of the long immersion time of twelve minutes. A coating consisting largely of alloy appears to have been aimed at, but the poor corrosion resistance is in any case difficult to understand.

Hot dip aluminised sheet has excellent resistance to heat, and is now in use for a wide range of articles where this property, together with some resistance to corrosion, is required. Such uses include exhaust systems for cars, ducting for air-heating systems, oven linings, etc.

The published information on corrosion resistance previously reviewed does not contain sufficient data obtained by means of special experiments with deformed and scratched specimens, including aluminised sheet with cut edges. The conclusion may be drawn that aluminised coatings are highly resistant to atmospheric corrosion, and are suitable in the humid and sulphurous atmospheres in which zinc is liable to greatly increased attack. On the other hand, the occurrence of uncoated spots is a much more serious matter than with hot galvanised coatings; the problem of cut edges, though serious, is probably easier to deal with.

Experimental Work

In order to obtain further information on the variables of the process, work has been carried out by B.I.S.R.A. since 1949, first on the laboratory scale and later with a small "pilot" plant for the continuous aluminising of strip and wire.

An examination has been made of the results obtained when cold-reduced mild steel sheet is dipped into molten aluminium after various preliminary treatments. The aluminium bath has been used over a range of temperatures, and its composition has been varied. The aluminised samples have been examined for coating thickness and structure, and the resistance of the coating to deformation has been tested. On the basis of the results obtained in this preliminary work, experiments have since been carried out on a larger scale, using a batch process for small samples of fabricated materials, such as tubes and rolled sections, and a continuous process for strip and wire.

(a) The Preparation and Protection of the Steel Base

Pickling

The steel used for laboratory work was mainly cold-reduced mild steel sheet of 23 s.w.g. (0·024 in.). The initial experiments were made with strips approximately 3 in. × $\frac{3}{4}$ in., suitable for an alternating bend test, but later work was carried out with small panels, 3$\frac{1}{2}$ in. × 2$\frac{1}{2}$ in., which were lightly oxidised in a muffle, pickled and dried. The oxidation was intended to remove oil residues and to avoid any difficulty in the pickling and fluxing operations. Uneven pickling had sometimes been observed with steel which had previously been degreased. Steel specimens of 15/16 s.w.g. (0·068 in.) and $\frac{1}{4}$ in. thickness were also used. Pickling was carried out either in 10% sulphuric acid (w/v) at 80° C. for three minutes, or in

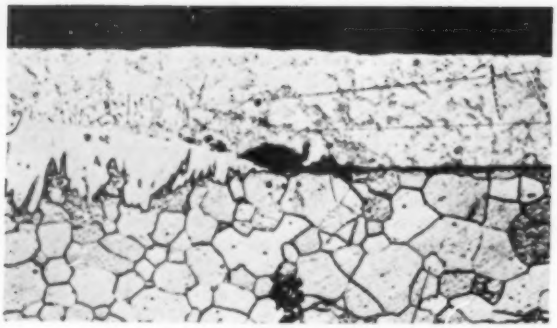


Fig. 1.—Local failure to alloy in a pure aluminium bath after gaseous pre-treatment. × 250

50% hydrochloric acid at 20/25° C., and the samples were then rinsed and, if necessary, dried.

Fluxing and Preheating

The pickled and dried samples were then immersed in a molten flux bath containing sodium and potassium chlorides with varying additions of zinc chloride, calcium chloride, sodium fluoride or mixtures of these. A proprietary flux recommended for the joining of aluminium was also used and gave fairly good results. The temperature of the flux bath was 650° ± 10° C., and the time of immersion varied up to three minutes, according to steel thickness. Prefluxing with a solution of zinc-ammonium chloride followed by drying was also tried, but was not entirely successful.

Preliminary Coating with Other Metals

As an alternative to the flux treatment, thin coatings of electrodeposited tin, zinc and cadmium were tried, but they gave erratic results. A thin coating of tin applied by chemical replacement from a molten tin salt was also unsatisfactory. Better results were obtained with samples dipped, after pickling and rinsing, in an acidulated solution of copper sulphate, and this simple method was later used on a larger scale with good results.

These metallic films are intended merely to prevent oxidation of the steel surface during immersion, and not to play any active part in the coating process. It has been found that a pickled and dried sample of mild steel sheet can be completely coated without the use of any fluxing process whatever, provided that it is immersed quickly, and that the temperature and time of immersion are increased somewhat. In continuous processing of strip and wire, conduction of heat up the ingoing strip leads to oxidation, and some form of protection is essential. A film of copper has been found to give satisfactory results in continuous processing, but the danger of reduced corrosion resistance due to increasing amounts of copper in the bath, later led to this method being considered unsuitable for material intended for resistance to corrosion. The good resistance to heat possessed by aluminised coatings would probably not be seriously affected unless simultaneous corrosion by condensate occurred—as for example in silencers for motor cars.

The Use of Protective Atmospheres

The use of mixtures of hydrogen and nitrogen, in varying proportions in an enclosure at the inlet to the aluminising bath, gave surprisingly unsatisfactory results. The coating was visibly imperfect, and even at areas which appeared to be well coated, microscopic examination revealed places at which alloying was imperfect or absent (Fig. 1). In an attempt to improve the results, hydrogen chloride was introduced into the atmosphere, but the result was not encouraging.

Preliminary Films of Glycerol and Similar Liquids

In the continuous aluminising of strip and wire, the protection against oxidation previously afforded by the thin film of copper has since been obtained by means of a film of glycerol. The use of alcohol as a flux is known, but the high temperature of operation in aluminising called for a liquid of higher boiling point. Further details will be given when discussing the aluminising of strip and wire.

(b) Dipping Conditions

Pure aluminium coatings were prepared in a bath made from "Super-Pure" aluminium (99·99% +). Additions of silicon were made in the form of a commercial aluminium silicon alloy containing about 11½% silicon. Additions of chemically pure zinc were also made. The temperature of dipping was varied from 675° C. to 775° C. in steps of 25°, when using pure aluminium. After the addition of silicon, lower temperatures (660° C. and 630° C.) were tried, and in experiments using the molten flux bath its temperature was reduced to 600° C. Immersion times of 10, 20, 30 and 60 seconds were used, increased to one and two minutes for steel ¼ in. thick.

The samples were withdrawn slowly, and were either cooled in air or, in other cases, quenched in warm water after the coating had solidified. (Air-cooled samples removed at high temperatures from a pure aluminium bath would be liable to have slightly more alloy than the corresponding quenched samples, but, owing to the extremely irregular inner boundary of the alloy layer in such samples, conclusive evidence of this was not obtained). The rate of removal with small strips and panels was not under precise control, which means that the outer layer was liable to vary in thickness: slow withdrawal minimised this danger. With the larger samples used in later work, a value is obtainable for withdrawal rate, and in continuous aluminising the speed is known and variable.

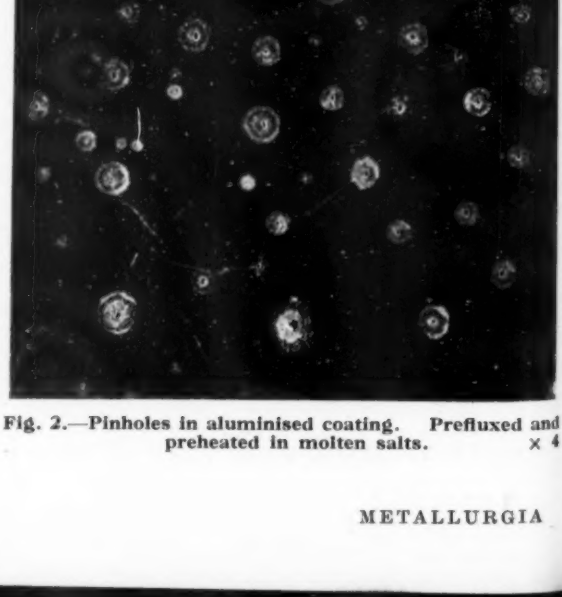


Fig. 2.—Pinholes in aluminised coating. Prefluxed and preheated in molten salts. × 4

(c) RESULTS

Appearance

Using the prefluxing and preheating technique, smooth and lustrous coatings were obtained, but these were often marred by small pinholes (Fig. 2). These pinholes were attributed to the flux which, as a result of continued use, is liable to contain particles of basic decomposition products, e.g., in the presence of zinc chloride; these would not melt off the steel surface owing to their higher melting point and, possibly, adhesive character.

On the other hand, omission of the flux produced coatings which were much less lustrous and were liable to be rough and to have nodules of bath metal adhering to the surface. The diminished lustre was due to greater oxidation of the film of molten aluminium, which was not protected by a thin film of flux during the withdrawal of the sample. The roughness was mainly due to the well-known tenacious character of the thin film of oxide which covers the bath. When broken up by the emerging sample, portions of the oxide film, with some entangled bath metal, sometimes produced unsightly nodules. Strip or wire which was withdrawn continuously and smoothly from the bath was generally free from nodules, the surrounding oxide skin remaining unbroken. An increase in iron content of the aluminium bath, or of the flux bath when used, also appeared to be a source of roughness.

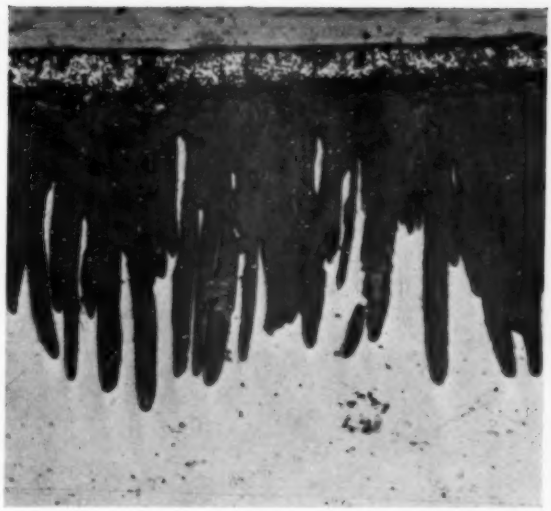
At dipping temperatures higher than about 770° C., using sheet samples as described and an unalloyed bath, alloy growth continues during withdrawal until it reaches the surface, and the product is then a dark grey colour.

Coating Thickness

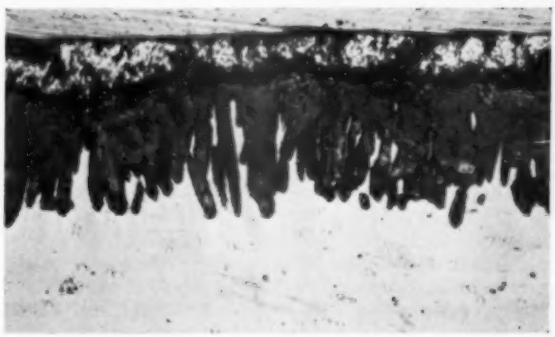
As in galvanising, the coating thickness increases with time and temperature of immersion due to growth of the alloy layer. The addition of silicon greatly reduces the rate of this growth. With a pure aluminium bath, the growth of alloy is so rapid that thin coatings, suitable for deformation, can be produced only at the lowest temperatures and with short times of immersion. Taking the mean of the two faces of panels aluminised after hot fluxing, a coating of about 1·5 oz./sq. ft. of sheet was obtained after 10 seconds immersion at 700° C. At 750° C., and with 30 seconds immersion, this value was approximately doubled. Using a bath alloyed with 2·8% silicon, a temperature of 695° C., and an immersion time of 10 seconds, a coating weight of 0·8 oz./sq. ft. of sheet was obtained—rather more than half that obtained without silicon. Increasing the temperature to 750° C. and the time to 30 seconds caused an increase of only 0·27 oz., to 1·07 oz./sq. ft., compared with an increase of 100% without silicon.

These results apply only to smooth cold-reduced sheet and depend also upon the rate of withdrawal. With short lengths of gas piping, rolled sections, and similar material having a rougher surface, thicker coatings were produced. Values of coating thickness and its variation are given in Tables III to VII for such material after batch aluminising and for continuously coated strip and wire.

Values given in oz./sq. ft. of surface or sheet are much lower than those obtained in hot galvanising, due to the



(a)



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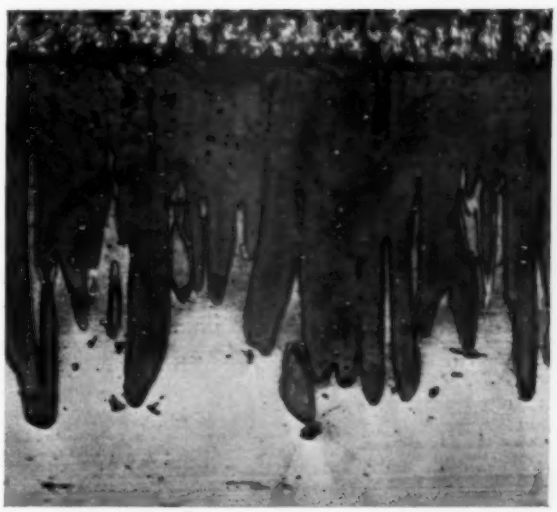

(c)

Fig. 3.—Rate of growth of alloy in pure aluminium bath at a dipping temperature of 725° C. Immersion time: (a) 1 minute; (b) 20 seconds. The structure shown in (c) indicates the presence of more than one alloy phase. × 400

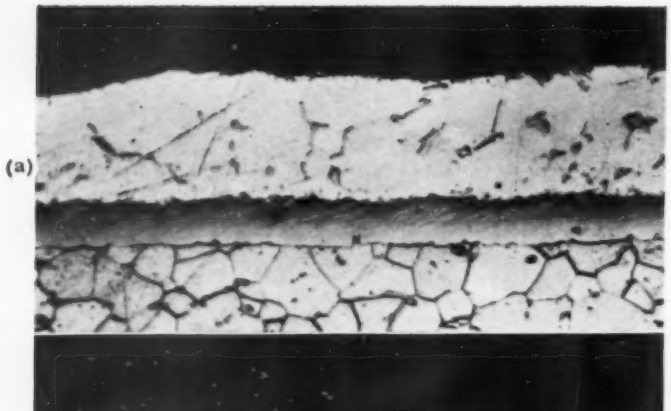

Fig. 4.—Influence of silicon on alloy formation. Bath temperature: 675° C.; time: 20 seconds; silicon content: 2·84%. Note difference in thickness of the outer layer of these samples, which leads to different bending properties (see Figs. 11a and 11b). × 500

lower density of aluminium. Calculation of thickness from the weight of a coating must take into account the presence of an appreciable thickness of alloy high in iron and denser than pure aluminium. An approximate conversion factor can be obtained by taking the relative density of the alloy as 4·0. A coating 1 mil thick, having an alloy layer equal to a quarter of its total thickness, would represent 0·50 oz./sq. ft. of sheet. A zinc coating of this thickness would have 1·2 oz./sq. ft. of sheet. (When coating weight is expressed in terms of surface, as in the coating of wire, these values should be halved).

Coating Structure

The total coating thickness is made up of a complex alloy layer adjacent to the steel base, together with an outer layer of the composition of the bath. When the bath has not been specially alloyed with silicon or beryllium, the alloy layer is likely to constitute the major portion of the coating thickness, unless the time and temperature of immersion are kept to a minimum. The aluminium diffuses rapidly into the steel on an irregular front as shown in Figs. 3*a* and 3*b*.

It is customary to refer to this alloy layer as $FeAl_3$ or Fe_2Al_5, but it is probably made up of the three alloys *zeta*, *eta* and *theta*, in order of diminishing iron content. The *theta* alloy, i.e., $FeAl_2$, is said to change into Fe_2Al_7 after solidification. Fig. 3*c* suggests that three alloy constituents are present, one occupying by far the greatest proportion of the thickness. According to Alferieff, the "alloy layer" produced in a bath of aluminium of commercial purity consists of (*a*) a solid solution of aluminium in iron; (*b*) a layer containing Fe-Al and $FeAl_2$; (*c*) an unidentified phase, probably $FeAl_2$; and (*d*) the phase $FeAl_3$. The existence of *zeta*, *eta* and *theta* phases in the alloy layer of coatings produced from pure aluminium was confirmed during unpublished work by the Research and Development Division, Carnegie Illinois Steel Corporation[11]. H. Röhrig[8] has described hot dipped aluminium coatings as made up of four layers, including the steel base. The alloy layer is described as $FeAl_2$ with "mixed crystals," i.e., a solid solution, below it.

When increasing amounts of silicon are added to the bath, the thickness of alloy is greatly reduced and its hardness diminishes[11]. With an addition of 2·84% silicon, the structure is as in Figs. 4*a* and 4*b* for the given conditions of immersion. These two samples show how the thickness of the outer layer may be affected by other factors such as speed of withdrawal, or drainage. This has a bearing on the bending properties as shown later. Further additions of silicon again reduce the amount of alloy, but the effect is less marked. When the silicon reaches the value of 11·4%, even the high temperature of 750° C. and immersion for 8 minutes do not produce an excessive thickness of alloy layer (Fig. 5). When the alloy is suitably etched (Fig. 6), an inner layer becomes clearly visible which appears to be a two-phase structure. Such two-layer alloy structures are seldom clearly seen after acidic etching, but on etching with

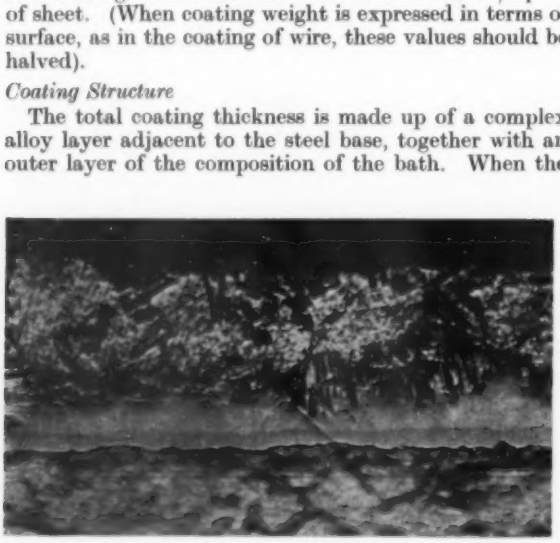

Fig. 5.—Thickness of alloy layer after 8 minutes at 750° C. in a bath containing 11·4% silicon. Etched with nitric acid in amyl alcohol ("nitramyl"). × 500

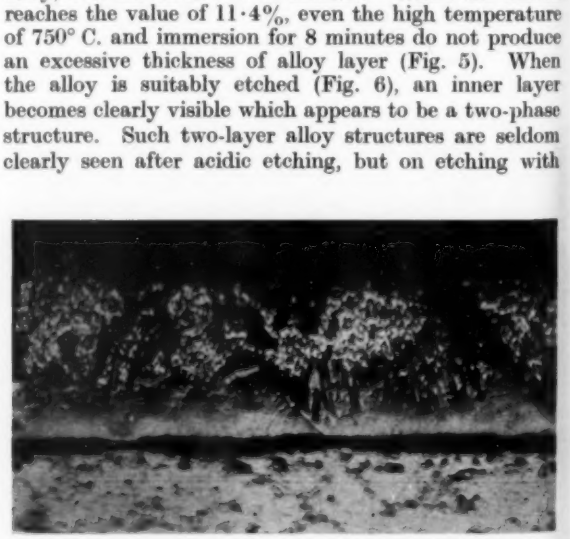

Fig. 6.—As Fig. 5, but etched with 5% caustic soda. × 500

warm 5% caustic soda they are revealed as a brown layer and a blue layer adjacent to each other. The exact result depends upon the bath composition and the conditions of dipping. Some evidence was obtained of the existence of a thin layer of alloy between the steel and the layer referred to above as the "inner" layer (Fig. 7).

The structure of Armco-Aluminised sheet, the product of a continuous process, is discussed under "Continuous Aluminising of Strip and Wire."

The Hardness of the Alloy Layer

Values for the hardness of the alloy layer have been given by Gittings *et al.*[11], who used a Knoop micro-indentor and a load of 25 g. The value of 900 is given for the alloy from a silicon-free bath, and with additions of 0·75%, 1·5%, 2·25%, 3·0%, 3·75% and 6% silicon, the average hardness diminished to 792, 792, 742, 661, 339 and 340 respectively. Much smaller additions of beryllium caused a similar rapid drop in hardness, though little further advantage appeared to be gained with more than 0·7% beryllium.

Our own work on the hardness of the alloy has been carried out with a Bergsmann micro-indentation tester, using loads of 20, 50, 100 and 200 g. On taper sections a series of micro-indentations have been made across the width of the alloy layer. It has been found that the hardness increases with distance from the steel/alloy interface. This is somewhat surprising and quite different from the results obtained with hot galvanised coatings. The iron-zinc alloy layers, *delta* and *zeta*, are clearly defined, differ appreciably in hardness, and the harder alloy is adjacent to the steel base. The iron-aluminium alloy layers show a more gradual change in hardness, and the maximum hardness is some distance from the steel.

The hardness of the alloy in silicon-free coatings is given as 900 by Gittings and Rowlands, but our tests, carried out on both perpendicular and taper sections, have given lower values. Loads of 25, 50, 100 and 200 g. have been used, and the average result is 610. This is unexpectedly low, and even when the two lowest results are discarded, to guard against error due to proximity of the steel base, the average is still only 625. No explanation has yet been found for this difference.

Fig. 7.—Additional thin layer of alloy at steel surface. Etched with 5% caustic soda. × 500

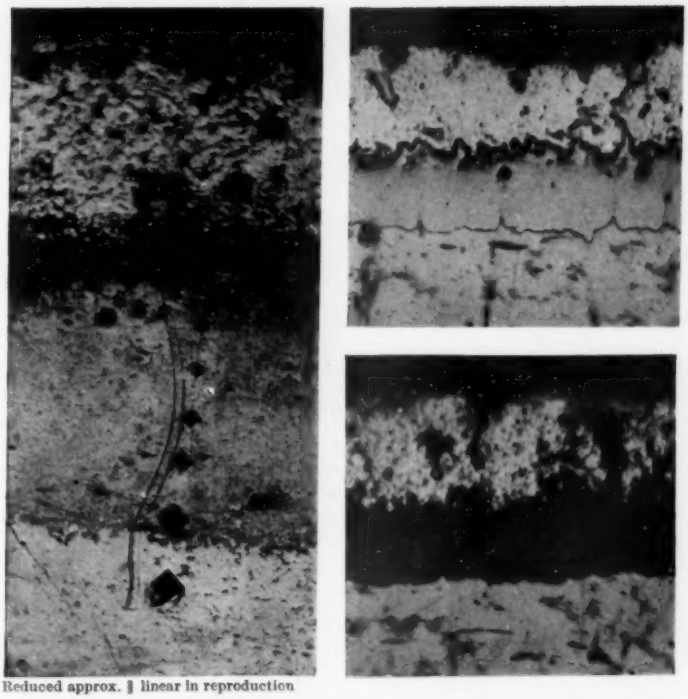

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Fig. 8a (left).—Taper section of aluminised coating showing variation of hardness across the alloy layer. 2·84% silicon bath. ×150

Fig. 8b (top right).—Perpendicular section of same sample etched with "nitramyl." × 500

Fig. 8c (bottom right).—As (b), but etched with 5% caustic soda. × 500

Fig. 8*a* shows the variation in hardness across the alloy layer of a coating containing 2·84% silicon. Figs. 8*b* and 8*c* show the structure in perpendicular section, etched with an acidic and an alkaline reagent respectively. When an indentation is very near to the steel base, the result may be low due to the presence of steel immediately below the spot tested. In order to simplify the measurement of the indentations, the tests were carried out before etching with alkali. The specimens were polished mechanically. Similar tests were made with coatings containing 4·84%, 6·8%, 7·5% and 11·4% silicon. The temperature of immersion was 750° C. in each case, to promote alloying, and the time was 30 seconds, except for the sample having 11·4% silicon, which was dipped for 8 minutes.

The results given in Table II show that, as in Fig. 8, there is an increase of hardness with increasing distance from the steel base.

Although it is not, perhaps, legitimate to average the hardness values of the two zones, this has been done in order to obtain an "average value" for the whole alloy layer. A comparison may then be made with the

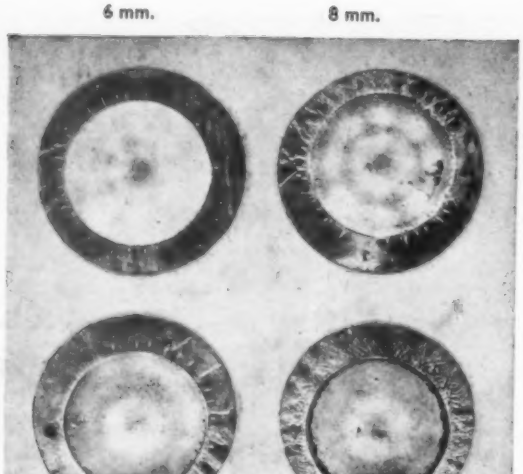


Fig. 9.—Erichsen adhesion tests on hot dip aluminised sheet (pure aluminium bath—copper pretreatment). Note development of peripheral cracking when test reaches 11 mm. × ⅔

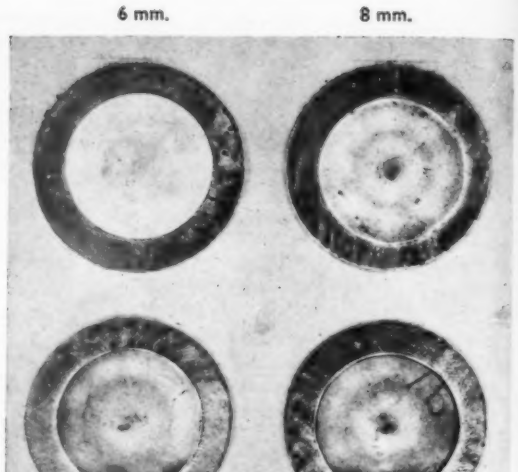


Fig. 10.—Erichsen adhesion tests on hot dip aluminised sheet (pure aluminium bath—glycerol pretreatment), showing good result obtainable. × ⅔

(a) Sample 181 flaked after two bends over 0·10 in. radius.

(b) Sample 90 showed only cracks after nine bends.

Fig. 11.—Difference in bending behaviour of two coatings produced under the same bath conditions but having different thicknesses of outer layer (see Figs. 4a and 4b). × 250

"mean" values given by Gittings *et al.*[11] for various silicon contents, which have already been quoted. Although our value at 2·84% silicon (671) agrees with 661 at 3% silicon, the sudden fall in hardness between 3·0 and 3·75% silicon was not detected. On the other hand, our results show a softer alloy at 7·5% silicon than the minimum value of 340 which they obtained with 3·75% silicon and again with 6% silicon. Although such tests are subject to some scatter, the differences discussed are large, and the marked drop in hardness may have an important effect on the behaviour of the alloy under deformation, such as bending and cupping.

Bending Properties

For many applications, the coating must withstand a certain amount of deformation. Sheet samples prepared in the laboratory and in a continuous unit have been examined by simple bending over various radii, by means of a Jenkins Alternating Bend Tester, and with two types of Erichsen machine. Samples of aluminised tube have been pressed flat, and wire has been subjected to wrapping tests over various radii.

The result obtained depends, as would be expected, upon the coating thickness and its structure. The latter depends in turn upon the composition of the bath, the presence of silicon having a marked effect as previously shown. To obtain coatings with good bending properties

TABLE II.—HARDNESS VALUES OF ALLOY LAYER BY MICRO-INDENTATION

Silicon %	Inner Zone	Outer Zone	Mean
(*a*) 2·84	480 (5)	862 (3)	671
(*b*) 4·84	386 (6)	744 (6)	565
(*c*) 6·8	245 (6)	534 (9)	390
(*d*) 7·5 (i)	162 (4)	364 (3)	263
(ii)	193 (3)	331 (3)	262
(*e*) 11·4	302 (1)	561 (6)	432

100 g. load for (*a*), (*b*) and (*c*), 50 g. load for (*d*) and (*e*). Numbers in bracket indicate number of results averaged.

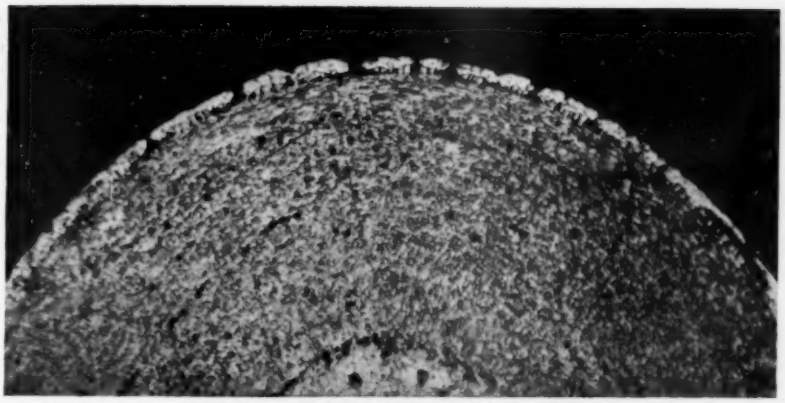
from a pure aluminium bath, the time of immersion must be short (e.g. 10 seconds) and the temperature low (e.g. 700° C.). If, in addition, the outer layer is thin as the result of slow withdrawal, the coating behaves very well in the alternating bend test, though not as well as a correspondingly thin zinc coating. Aluminium coatings appear to fail early under compression, but withstand tension much more successfully. This makes an alternating bend test relatively more severe, for the surface subjected to tension in the second bend has already suffered compression during the first bend. This may lead to the presence of minute cracks, which may initiate wider cracks or even flakes on the next bend. Aluminised sheet bent over a $\frac{1}{16}$ in. radius and then squeezed in a vice showed no "flakes," the coating behaving as shown in Figs. 12*a*, 12*b* and 12*c*.

The relative resistance to tension and compression is also seen in the standard Erichsen test. Flaking of the coating on the dome, as encountered in many zinc coatings, does not occur, but cracking may appear around the base of the dome, as in Fig. 9. At this position, there is a combination of bending and compression as the sample passes through the die. Along the "flanks" of the Erichsen dome the sample is under tension, and coating failure does not normally occur there. That good results are obtainable with pure aluminium coatings is shown by Fig. 10.

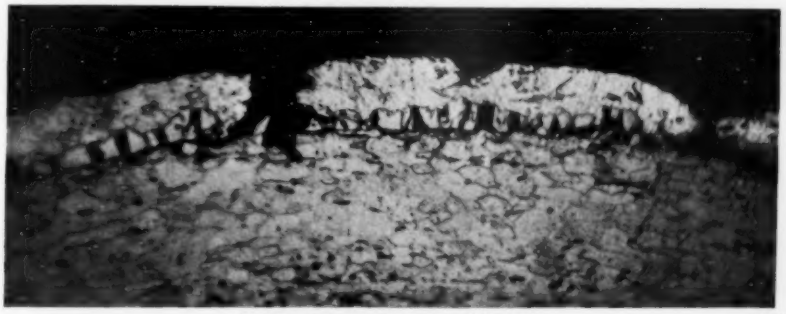
The addition of silicon to the aluminising bath improves the behaviour of the coating in cupping and bend tests. This is no doubt due to the marked change in alloy structure and the reduction in its hardness. It is still advisable to keep the outer layer fairly thin. The coatings shown in Figs. 4*a* and 4*b* behaved differently in the bend test, as shown in Figs. 11*a* and 11*b*, and this difference is due to the greater thickness of outer layer of sample 181 : hot galvanised coatings behave in the same way.

A further difference between aluminium and zinc coatings is seen in Figs. 11*a* and 11*b* and in Fig. 13*d*. The plane of failure is seen to lie in the alloy layer, which is badly shattered, whereas a flake in a zinc coating is almost always a clean separation between the alloy layer and the steel.

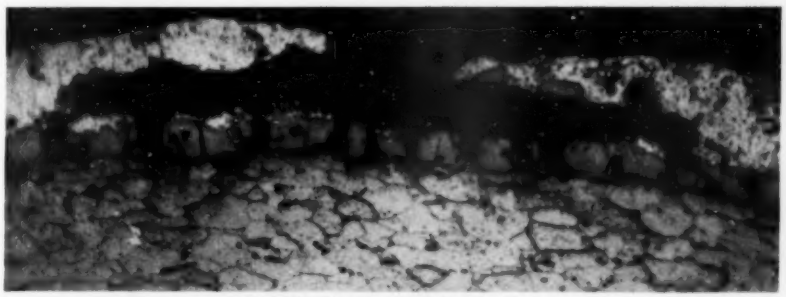
Although the addition of a small amount of zinc (e.g. 1%) to the aluminising bath had no detectable effect on the alloy layer produced, the behaviour of the coating in the bend test appeared to be improved. The use of zinc was not continued, because additions of zinc sufficient to cause a useful fall in operating temperature resulted in abnormally thick coatings. (A similar vigorous reaction between the bath and the immersed steel was observed when heavy additions of aluminium were made to galvanising baths.)



(a) General appearance at apex of bend. × 80



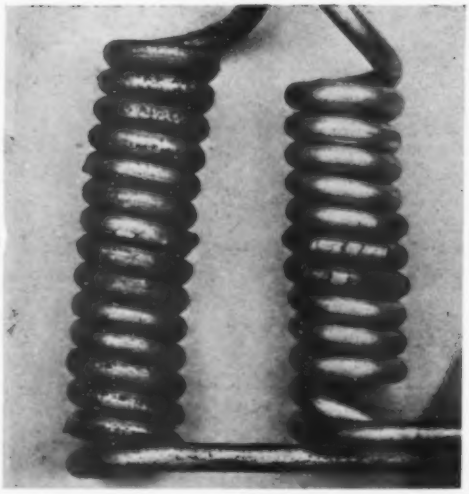
(b) Structure at apex of bend. × 500



(c) Behaviour at right of (a). × 500

Fig. 12.—Bending behaviour of continuously aluminised $\frac{1}{2}$ in. wide strip.

Wrapping tests on continuously aluminised wire have not always yielded satisfactory results. Since coatings continuously applied to strip in the same bath under the same conditions gave good results on bending, as shown in Figs. 12*a*, 12*b* and 12*c*, it was concluded that wire required a more elaborate preparation for coating. Control of coating thickness also enters into this problem. The wrapping test shown on the left of Fig. 13*a* gave a poor result due to the excessive thickness shown in Fig. 13*b*. The test on the right gave an excellent result except for three turns at



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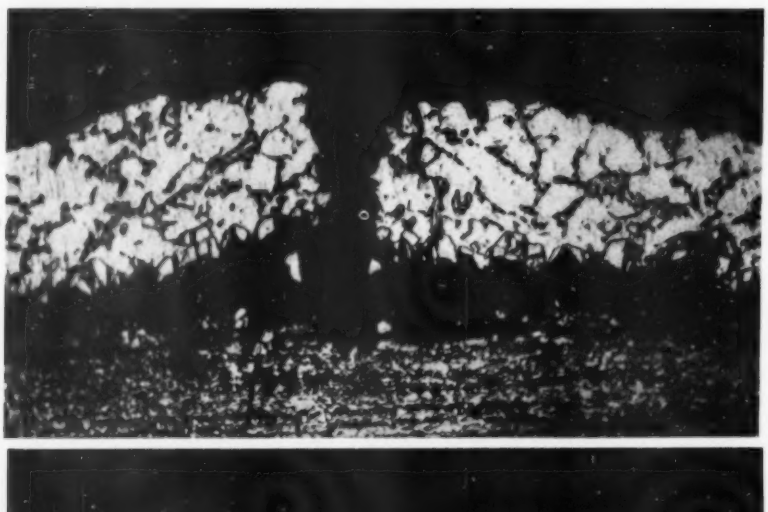

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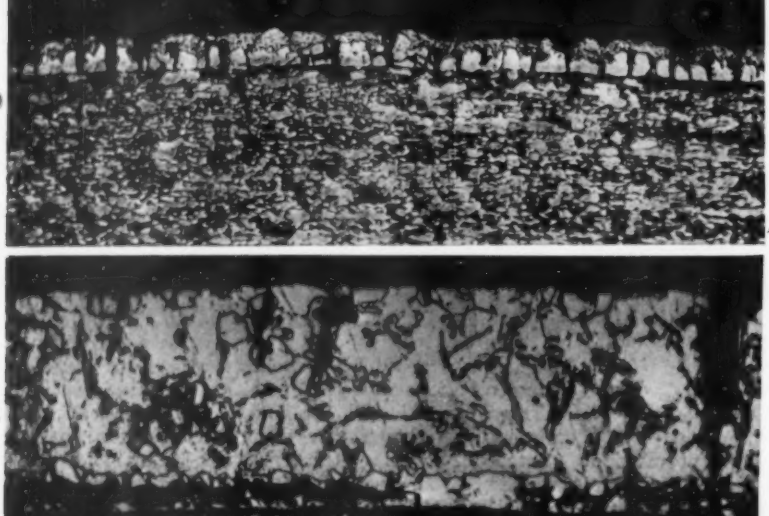
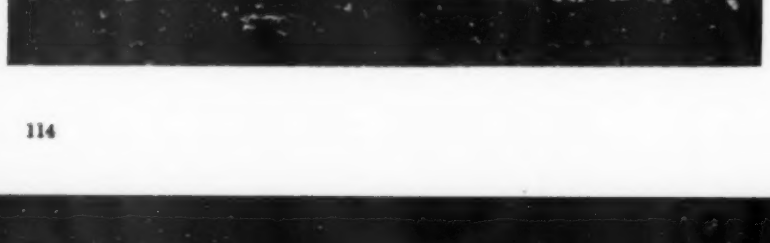


(c)



(d)

Fig. 13.—Influence of coating thickness on wrapping tests on continuously aluminised 17 s.w.g. wire.

(a) Left : unsatisfactory. Right : locally unsatisfactory region. × 3

(b) Thick coating of unsatisfactory wire. × 300

(c) Thin coating of satisfactory wire. × 300

(d) Thicker coating at poor region of wire (c). × 300

the centre—which also have the darker appearance of the left sample. Figs. 13*c* and 13*d* show that this local failure is due to a local thickening of the coating. Both wrapping tests were carried out on the same coil. This suggests that with a suitable arrangement for "wiping," the coated wire should give better bending results. Simple wiping devices using asbestos cord have not yet given consistent results.

Corrosion Resistance

Insufficient time has elapsed for the specimens prepared during this work to be tested adequately for resistance to atmospheric corrosion. Experiments have been carried out, however, to examine the special properties associated with hot dip aluminised coatings. Resistance to humidity is said to be greater than with zinc coatings which fail rapidly due to formation of white rust. Small panels coated with aluminium of commercial purity and with additions of 1½% and 3% silicon, together with companion samples of good quality galvanised sheet, were tested by suspending them over water which was heated during the day and allowed to cool overnight. After 12 days, the galvanised panels were dark and had developed some white rust; the aluminium coatings appeared unchanged, except that a bare spot on one panel had rusted. (Fig. 14*a*). After 148 heating and cooling cycles,* and, in addition, about 60 days at weekends during which no heating occurred, the galvanised panels were somewhat darker, but the aluminised panels had suffered very little change except at bare spots, which were now much more conspicuous. (Fig. 14*b*). Identification marks written on the aluminised samples were found to be still perfectly legible.

Sample No. 5 in the above test was chosen to see the behaviour at a bare spot. A larger panel, which had been cold rolled after coating with pure aluminium, and which had some bare spots, was exposed to the atmosphere for the same reason. This panel and its companion galvanised panel both had coatings about 1½ mils thick. After 454 days exposure to the Swansea atmosphere, their appearance was as shown in Fig. 15. The corrosion product at the bare spots of the aluminium coating had spread

*This test was continued for 291 cycles and the samples appeared to suffer no further change.

into unsightly patches. The actual area which rusted is probably much less, and the appearance is somewhat misleading[25]; such localised attack is likely to lead to perforation.

The failure of hot dip aluminium coatings to protect cut edges applies to both pure aluminium coatings and those alloyed with silicon. Samples immersed in Swansea tap water at room temperature had loose iron hydroxide at the cut edges within a few hours; the attack was visibly less in distilled water. Samples of galvanised sheet immersed in both waters showed no sign of rusting after three days, but had a characteristic greyish white surface film. When the corrosion product was removed from all the samples (by swabbing only), the loss of weight of the galvanised samples was found to be greater than that of the aluminised samples. This illustrates the difficulty of assessing the degree of attack by visual inspection. (This type of experiment does not indicate the long term behaviour of the two coatings. The initial attack on the zinc coating leads to the formation of a protective film, whereas the attack on the cut edges of the aluminised samples is liable to be progressive if the product is non adherent). It may be noted here that in the Aeronautical Material Specification for aluminised sheet and strip, drawn up by the American Society of Automotive Engineers[29], a salt-spray test is included, and it is stated that "corrosion of basis steel at cut edges shall be disregarded."

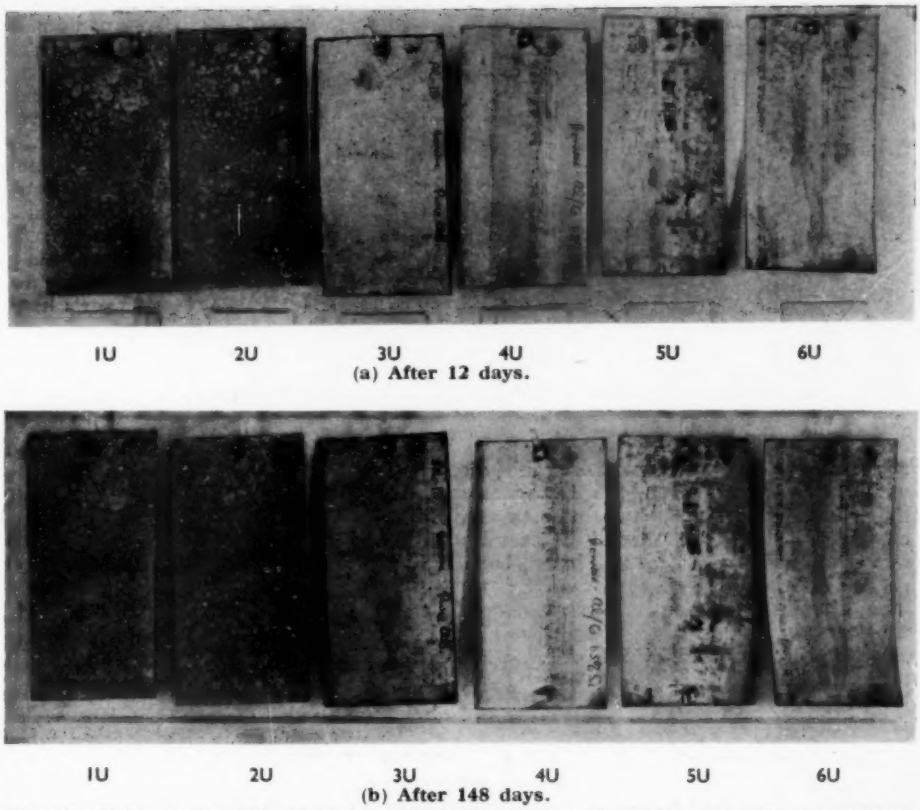


Fig. 14.—Galvanised and aluminised panels after exposure to humidity tests. Nos. 1 and 2 are galvanised and the remainder aluminised; No. 3 in pure aluminium, No. 4 in a 1½% silicon bath, and Nos. 5 and 6 in a 3% silicon bath. × ½

Heat Resistance

Preliminary experiments have been carried out to determine the heat resistance of aluminised sheet and wire. Specimens, 3 in. × 2 in. × 0·023 in. of plain steel, and of the same steel coated with commercial quality aluminium and with aluminium containing 5% silicon were heated for 2,000 hours in a vertical position in a muffle at 500° C. The plain steel scaled freely and lost 1·24 g. in weight; the specimen coated with aluminium developed a characteristic dark colour due to the growth of alloy to the surface, but the change in weight was merely a gain of 8·7 mg. The silicon-alloyed coating suffered no visible change, except at

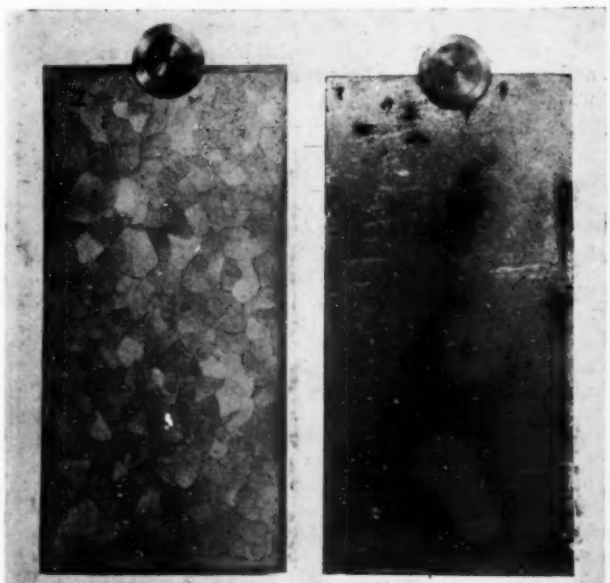


Fig. 15.—Panels after 454 days atmospheric exposure at Swansea. The left-hand panel is hot dip galvanised and the right-hand panel is hot dip aluminised and cold rolled. × ½

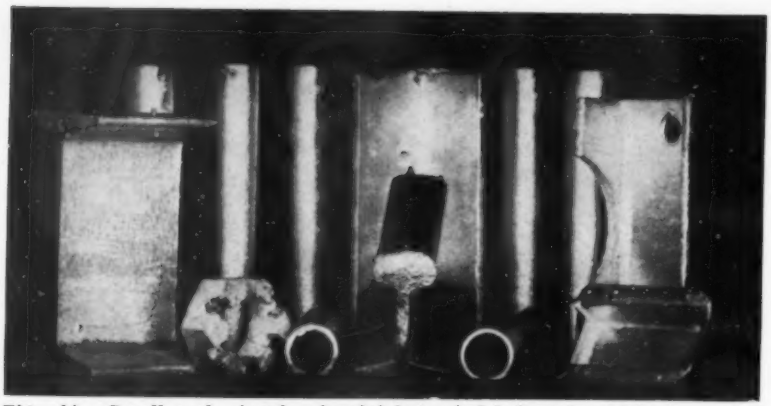


Fig. 16.—Small-scale batch aluminising of fabricated articles. × 2/7

small areas which were somewhat thinly coated, and which darkened due to the appearance of alloy. The change in weight of this sample was even less, a gain of 6·6 mg. Similar sheet samples are being tested at 600° C. After 1,500 hours, both aluminised coatings were in excellent condition: those with a plain aluminium coating had gained about 22 mg, and those with silicon-alloyed coating about 15 mg. Results with 10 s.w.g. and 16 s.w.g. wire have been similar.*

The Small Scale Batch Aluminising of Fabricated Articles

The laboratory work on the hot dip aluminising of sheet samples was followed by work on a larger scale using samples of steel tube, angle iron and other rolled sections, up to 15 in. in length. The preparation of the samples was similar to that previously described, viz. pickling in hot sulphuric acid, rinsing, and the application of a copper film. Dipping time was varied with the thickness of the section concerned, and the bath temperature was kept within the range 700°–750° C. It was now possible to time the withdrawal of the samples, and so obtain a value for the speed of emergence, which was always low.

Appearance

The results were highly satisfactory for a variety of samples, bright attractive finishes being obtained as may be judged from Fig. 16. Short lengths of gas piping, 6 in. × 1 in. dia. × $\frac{1}{16}$ in. wall thickness, had an excellent appearance after dipping for 30, 45 or 60 seconds at 730° C., and for the same times at 700° C. Shorter times of immersion appeared to be inadequate, although even at 15 seconds only the upper portion was unsatisfactory. (Since withdrawal occupied from 6 to 9 seconds, dipping being vertical, the lower part of each sample had a longer immersion time). When panels of cold-reduced sheet (10 in. × 7 in.) were dipped, trouble was experienced with the formation of nodules of metal on the surface, in most cases on one face more than the other. Many of these nodules were too large to be dealt with by any subsequent cold rolling; examination showed them to be composed almost entirely of bath metal, but their formation and liquid stability was no doubt due to membranes of alumina, which were difficult to identify conclusively under the microscope. These nodules had previously been seen during laboratory work, and have been referred to earlier. When such panels were dipped by hand, it was difficult to withdraw the sample sufficiently smoothly to avoid oxide entanglement. There are two possible explanations of the absence of nodules on the tubes and rolled sections. The comparatively light and thin panel would respond more readily to any tremor of the dipper's hand, and would cause more disturbance of the surface than would the heavier and smaller length of tube or rolled section. Secondly, the much rougher surface of the sections causes a much greater drag-out of liquid metal and this, as it drains back into the bath, may be able to wash back any particles of adherent oxide which would be liable to lead to the formation of nodules. A modified method of dipping small sheets in order to eliminate these nodules will shortly be tried.

Coating Thickness

Magnetic tests on tubes etc., indicate that a fairly thick coating is applied when the surface is fairly rough, when compared, for example, with cold rolled sheet. The uniformity is very satisfactory and the protective value of such a coating should be very good. Eleven tests along an aluminised tube gave values varying only from 2·1 to 2·4 mils, and a mean value of 2·28 mils. A series of tests along a line diametrically opposite gave results from 2·0 to 2·4 mils, and a mean value of 2·22 mils.

Four rows of 11 tests carried out on the four faces of a 6 in. length of aluminised angle iron, 2 in. × 2 in. × $\frac{1}{4}$ in.,

TABLE III.—INFLUENCE OF IMMERSION TIME ON COATING THICKNESS ON ALUMINISED TUBES—PURE ALUMINIUM BATH

Tube No.	Time	Average Coating (mils)		No. of Tests	
		Along Line A	Along Line B	A	B
10	30 sec.	1·7	1·5	6	6
13	1 min.	1·9	1·95	6	6
21	2 min.	2·7	2·7	10	10
23	3 min.	3·1	3·1	10	10

Tubes 10 and 13, 3·6 in. × 1 in. diam. Tubes 21 and 23, 5 in. × 1·6 in. diam. Samples machined before dipping. Values determined by magnetic testing.

TABLE IV.—COATING THICKNESS ON TUBES ALUMINISED AS IN TABLE III BUT WITHOUT MACHINING THE SURFACE

Tube No.	Time	Average Coating (mils)		No. of Tests	
		Along Line A	Along Line B	A	B
4	30 sec.	2·4	2·5	7	7
3	1 min.	2·9	2·6	9	9
1	1 min.	2·8	2·9	9	9
2	2 min.	3·6	3·3	9	9

TABLE V.—COATING THICKNESS ON STEEL PANELS, 10 in. × 6 in. × $\frac{1}{4}$ in.

Samples	Coating Thickness by Magnetic Tests (mils)						Time of Immersion (minutes)
	Left Side		Middle		Right Side		
	Face A	Face B	Face A	Face B	Face A	Face B	
20	2·2	2·1	2·2	2·1	2·1	1·9	2
19	2·9	2·8	2·8	2·9	2·9	2·8	3
22	2·6	2·7	2·6	2·7	2·6	2·9	3

All values are means of 9 tests made in a straight line.

*Tests at 700° C. not yet completed, show that good results are obtained with both types of aluminised coating. The possibility that grain growth of the basis steel may lead to deterioration in physical properties is being examined.

gave the values 1·9, 2·2, 1·9 and 1·7 mils, using a different instrument having a dual scale. When the tests were repeated using the other scale, the values obtained were 2·0, 2·3, 2·05 and 1·8 mils. Three tests were made at each of the 11 points and the results averaged. Further details of coating thickness and its uniformity are given later. The influence of immersion time is seen in the results given in Table III.

In order to obtain maximum accuracy from the magnetic tests, these samples had been machined smooth before dipping. The extra smoothness is likely to cause a lower result, but the work put into the surface by machining could cause an increase in alloying action. Similar tubes to Nos. 21 and 23, aluminised the previous day in the same bath, gave higher results as shown in Table IV. Three flat rectangular samples, 10 in. × 6 in. × ¼ in., dipped in pure aluminium at 740° C. for 2 minutes (in 2 cases) and for 3 minutes, also gave very uniform results, although the coating was less smooth on these. The results are summarised in Table V.

Hot rolled window sections of different sizes were also dipped in pure aluminium in lengths of 12½ in. to 13¾ in. After immersion for 2 minutes at the somewhat high temperature of 760° C., coatings of 5½ mils to 7½ mils were produced on the rougher samples, and 4¾ to 5¾ mils on smoother surfaces. The appearance was bright and attractive though somewhat rough. (Since 1 mil represents only 0·25 oz./sq. ft. surface, these thick coatings require the expenditure of only 1 to 1¾ oz./sq. ft. of aluminium, even without any allowance for the appreciable amount of iron in the coating.)

The thickness values obtained by magnetic tests have been checked occasionally by chemical stripping and during microscopic work, and found to be within 10 to 15%. Panels have been tested at 5 points within circular areas which were later blanked out and stripped. Discs which gave "stripping" values of 1·36, 1·28, 1·35 and 1·50 mils, had previously given magnetic results of 1·26, 1·28, 1·22 and 1·26 mils. Magnetic results of 1·04 and 1·2 mils on the two faces of a sample compared with 1·18 and 1·4 mils by stripping.

Bending Properties

Although fabricated articles are not generally expected to withstand bending, this does not apply to tubes. Samples 1 in. long were, therefore, cut from aluminised tubes and pressed flat in an Amsler testing machine. The coatings did not flake but exhibited cracks of varying width; an example is shown in Fig. 17.

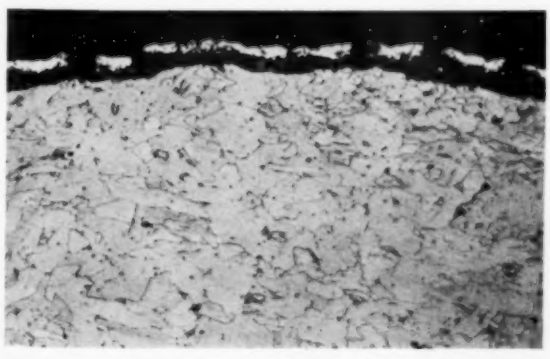
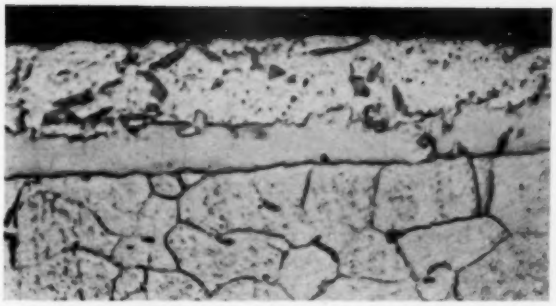


Fig. 17.—Compressed aluminised tube: behaviour of coating at bend. × 75



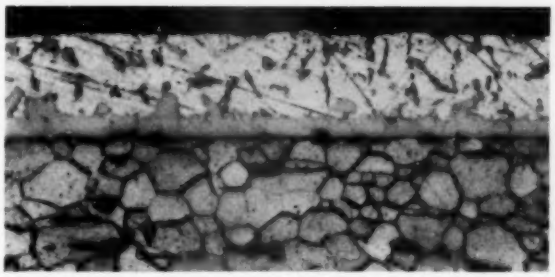


Fig. 18(a). (above)—Structure of Armco-Aluminised sheet. × 1000
(b). (below)—Structure of a more recent sample. × 500

"General Aluminising"

These experiments suggest that "general aluminising," on lines similar to "general galvanising," should not be too difficult a process to operate. Since bending properties are less important, pure aluminium baths could be used, which, by the more vigorous alloying action would reduce the danger of any uncoated areas. It would result also in thicker coatings with a greater life. The statement by A. Di. Guilio[18] that "inasmuch as the aluminium coating produced . . . is structurally similar to the coating produced in hot-zinc dipping, the process promises to be no more difficult to handle than is ordinary galvanising" is, however, distinctly misleading. The coating differs from galvanised coatings both in structure and in certain properties, and the process has certain inherent limitations and difficulties, largely arising from the higher temperature of operation. This leads to softening of cold-worked high tensile material, slight air hardening of thin material, and a greater tendency to warping when dipping fabricated articles containing residual stresses. The high temperature also leads to rather more discomfort for the operator and a higher fuel cost. Despite these factors, the process has merits, both economic and technical, which suggests that it has its own field of application. There are signs that this is now being appreciated in the United States[20, 21, 22].

The Continuous Aluminising of Strip and Wire

The outstanding industrial application of hot dip aluminising, possibly the only large-scale example, is the continuous aluminising of cold-reduced mild steel strip in Sendzimir units to produce Armco-Aluminised sheet. This process, which has been previously referred to, has been in commercial production since about 1939. The corrosion resistance of this material has already been discussed; its structure is shown in Figs. 18*a* and 18*b*, representing samples received a few years ago and a few

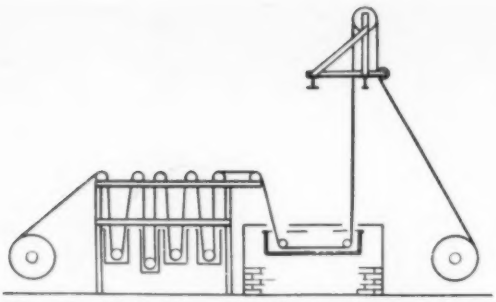


Fig. 19.—First pilot plant for continuous aluminising of strip and wire (1 in. equals approximately 7¼ ft.).

months ago, respectively. There does not appear to be any marked change in the structure during the interval, and the coating is uniform and thin. The alloy layer in particular is thin, and the behaviour in the Erichsen test is very good. The sheet has an excellent appearance, even when it is the "regular dull finish" and not the "extra-smooth" grade which is also made. The smooth lustrous surface is clearly the result of treatment subsequent to coating, and the S.A.E. specification previously referred to[29] calls for a re-rolling after coating.

The equipment used in this process is expensive and suitable only for continuous processing on a fairly large scale. The smaller manufacturer would require either a simpler and cheaper continuous unit, or a method of processing single sheets. The advantages of continuous processing are so obvious that a small pilot plant, suitable for the continuous aluminising of strip up to 2 in. width, or of wire, was erected in order to study this process.

Pilot Plant for Continuous Aluminising

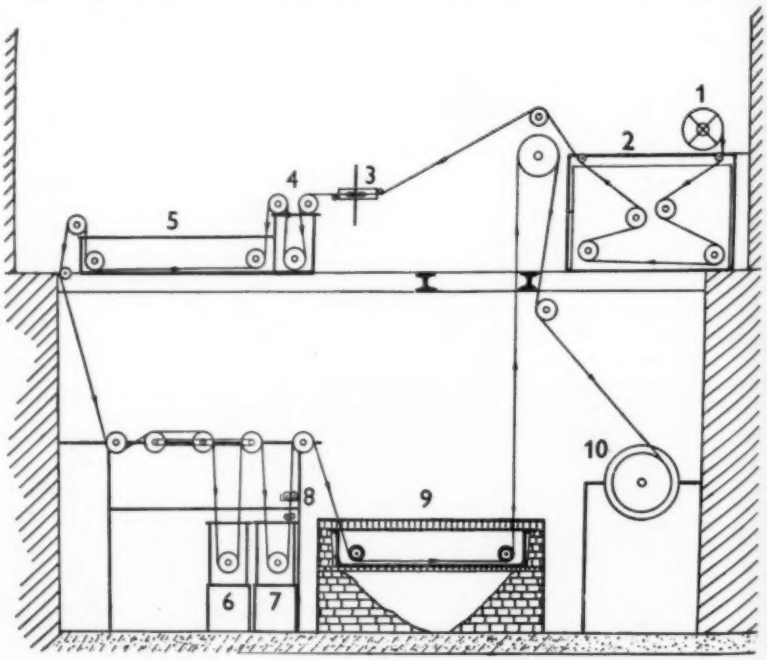
The main objective in this work was to reduce the process to the simplest form consistent with satisfactory coating. It had been observed that clean cold-reduced strip could be coated without any preliminary treatment of any kind, and advantage was taken of this when constructing the pilot plant. In its original form, the steel preparation section consisted only of two degreasing operations, using hot alkali and trichlorethylene, followed by arrangements for giving a thin "immersion" coating of copper, followed by a rinse. After drying, the strip or wire entered the molten bath, having an immersed path of 4 ft. 6 in., and passing through at speeds from 3 to 30 ft./min. On leaving the bath, the strip or wire passed vertically upwards for some distance and then downwards to a coiler: the arrangement is shown diagrammatically in Fig. 19. Operating speeds were generally 10 ft./min. or 20 ft./min. Beginning with a bath of 2 cwt. of commercially pure aluminium, additions of silicon up to 5% were made. The metal was contained in a pot, 48 in. × 12 in. deep × 5¼ in. wide, made of a cast iron which had previously been tested and found resistant to aluminium, and coated on the inside with a proprietary wash which gave very good results.

Coils up to 300 ft. in length were aluminised, sections of a coil being processed at different speeds. Good results were obtained with 2 in. wide strip, and later with ¾ in. strip, but some trouble was experienced with wires of different gauges. This was attributed to the need for more thorough preparation of wire, which is always liable to have a surface contaminated with films derived from drawing lubricants. The pilot plant was, therefore, modified so as to include a brushing and pickling treatment. This more elaborate arrangement is shown diagrammatically in Fig. 20.

A further modification was made when it was decided to omit the filming with copper, and to use glycerol or glycol instead. The two tanks for the copper sulphate solution and for rinsing were replaced by an arrangement of two rollers dipping into small amounts of glycerol which had been thinned with methylated spirits. The strip passed between these rollers (Fig. 20), which transferred a thin film of liquid to it. The glycerol ignited on meeting the molten bath, the strip at that stage being within a confined space. The whole unit has recently been altered to permit the coating of wider strip, up to 4 in. wide. The new pot is 5 ft. 0 in. × 17½ in. deep × 9 in. wide, and will hold 7 cwt. of aluminium.

The Appearance of the Product

The coils of coated strip and wire had a "bright matt" finish rather than a smooth lustrous appearance. Since the emerging strip is not at present protected in any way against oxidation, this finish is the one to be



1. DECOILER.
2. VAPOUR DEGREASER.
3. SCRUBBING BOX.
4. WASH TANK.
5. PICKLING TANK.
6. PICKLING TANK.
7. WASH TANK.
8. GLYCEROL APPLICATION.
9. FURNACE AND POT.
10. COILER.

Fig. 20.—Modified pilot plant (1 in. equals approximately 4½ ft.).

expected and is quite attractive. The nodules which occurred so often with hand dipping, were now relatively infrequent. (The first coil made was, in fact, almost free from such nodules). Roughness of a smaller order has occurred on several occasions on strip, and is one of the problems not yet completely solved. Any vibration of the strip leads to a marked rippling of the coating, and this trouble was encountered until some mechanical adjustments were made. A phenomenon resembling the "de-wetting" which occurs in hot tinning, and occasionally in hot galvanising, has been observed. The outer layer of the coating retracts from certain areas of the surface, leaving the alloy layer exposed (Fig. 21). Aluminised wire has usually been brighter and less liable to roughness than the strip, although, as previously stated, wire is more likely to give trouble with the coating process, leading to uncoated areas, unless thoroughly cleaned. An improved appearance is obtained when the strip is cold rolled after coating or the wire is cold drawn. In some cases this may not be permissible owing to the reduced ductility of the product.

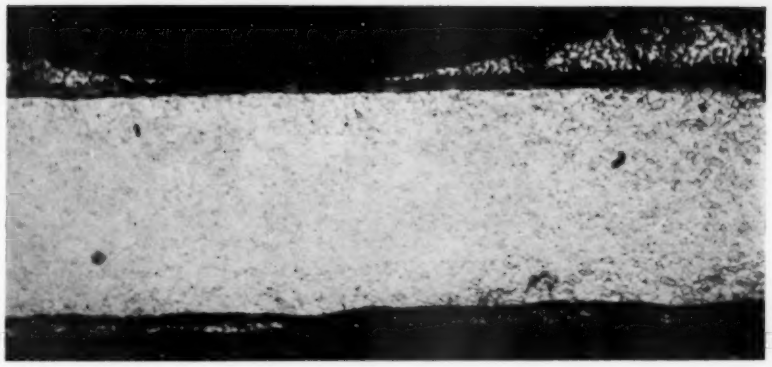


Fig. 21.—Retraction of outer layer of coating, exposing iron-aluminium alloy. × 70

Coating Thickness and Uniformity on Aluminised Strip and Wire

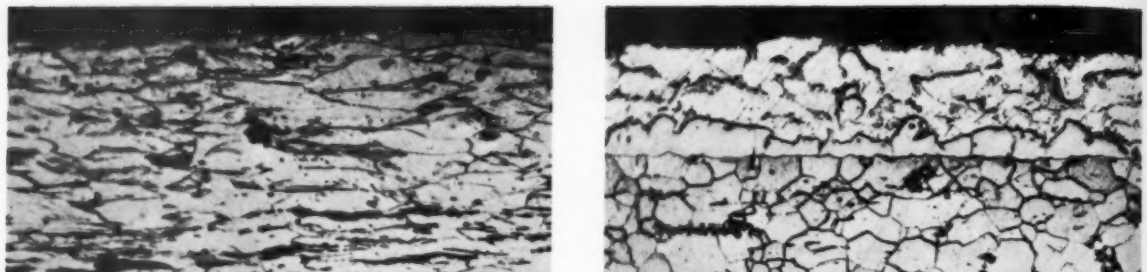
Examples of coating thickness variation along aluminised strip and wire are given in Tables VI and VII, respectively. The values for strip are given in oz./sq. ft. of sheet, as is customary in the sheet and strip galvanising industry. The values for wire are in oz./sq. ft. *of surface* and, for a given coating thickness, are half the values given for sheet or strip.

The results given in Table VI for aluminised strip show, by comparison of lines 1 and 2 the effect of strip speed, and, therefore, immersion time, on coating thickness. The bath is pure aluminium, and a higher speed means less immersion time and less alloying. The effect of silicon additions in reducing coating thickness is seen

TABLE VI.—COATING THICKNESS ON CONTINUOUSLY ALUMINISED COLD-REDUCED MILD-STEEL STRIP.

No.	Ref.	Speed of Strip (ft./min.)	Bath Composition	Temperature (° C.)	Sampled	No. of Samples	Coating Weight (oz./sq. ft. of sheet)			Mean Deviation
							Mean	Max.	Min.	
1	Al/14	3	"Pure" Aluminium	735	12 in. Intervals	12	2·68	2·94	2·46	0·12
2	Al/14	25	"Pure" Aluminium	735	12 in. Intervals	6	2·09	2·22	1·98	0·082
3	Al/19	12·8—Front	"Pure" Aluminium	760 (?)	6 in. Intervals	8	1·73	1·89	1·52	0·075
4	Al/19	12·8—Rear (70 ft. apart)	"Pure" Aluminium	760 (?)	6 in. Intervals	16	2·24	2·54	2·00	0·135
5	Al/6	10	1¼% Silicon	720	6 in. Intervals	17	1·48	1·73	1·26	0·011
6	Al/8	10	2·65% Silicon	710	6 in. Intervals	12	0·89	0·98	0·77	0·061
7	Al/20	3—Front	2·36% Silicon	—	12 in. Intervals	9	0·93	1·20	0·68	0·19/0·23
8	Al/20	3—Rear (125 ft. apart)	2·36% Silicon	—	12 in. Intervals	10	1·77	1·96	1·54	0·24/0·23
9	Al/22	6—Front	4·5% Silicon	740	12 in. Intervals	6	0·78	0·90	0·64	0·08/0·18
10	Al/22	6—Middle	4·5% Silicon	740	12 in. Intervals	6	0·66	0·69	0·59	0·06/0·05
11	Al/22	6—Rear (154 ft. apart)	4·5% Silicon	740	12 in. Intervals	6	0·68	0·74	0·63	0·03/0·06
12	Al/23	12—Front	5·4% Silicon	730	12 in. Intervals	6	0·76	0·83	0·70	0·15/0·05
13	Al/23	12—Middle	5·4% Silicon	730	12 in. Intervals	6	0·89	0·92	0·86	0·06/0·06
14	Al/23	12—Rear (227 ft. apart)	5·4% Silicon	730	12 in. Intervals	6	0·88	0·90	0·87	0·01/0·08
15	Al/24	12—Front (A)	5·4% Silicon	720	12 in. Intervals	3	0·66	0·68	0·64	0·05/0·06
16	Al/24	12— + 26 ft. (B)	5·4% Silicon	720	12 in. Intervals	3	0·77	0·82	0·72	0·018/0·04
17	Al/24	12— + 30 ft. (C)	5·4% Silicon	720	12 in. Intervals	3	0·65	0·66	0·64	0·09/0·10
18	Al/24	25—Front (E)	5·4% Silicon	720	12 in. Intervals	3	0·68	0·76	0·61	0·10/0·01
19	Al/24	25— + 10 ft. (F)	5·4% Silicon	720	12 in. Intervals	3	0·64	0·67	0·60	0·04/0·03
20	Al/24	25— + 10 ft. (G)	5·4% Silicon	720	12 in. Intervals	3	0·58	0·59	0·58	0·12/0·03

NOTES: 1. Lines 1 to 11 refer to strip 2 in. wide and 24–26 s.w.g. Lines 12 to 20 refer to ½ in. wide strip × 22 s.w.g.
2. From line 7 onwards, the mean deviation is given for upper and lower faces of the strip in each case. From line 9, the mean coating value used is that for all 18 samples in each group.
3. Lines 1, 2, 5 and 6 refer to coils treated with copper before aluminising; the others were given a film of glycerol.



(a) Hard rolled. (b) After aluminising.

Fig. 22.—Structure of mild steel strip × 300

in lines 5 and 6. On some occasions, coating thickness has appeared to increase towards the rear of the coil and this is illustrated in lines 3 and 4 (pure aluminium) and 7 and 8 (2·3% silicon), despite the slow speed of the latter. The results given for Al/22, Al/23 and Al/24 show that this upward drift in values towards the rear does not always occur, and that coating uniformity is generally very good. As with other hot dipping processes, there is a difference between the coating weight on the two faces.

Coating thickness values for wire are given in Table VII: coating uniformity is satisfactory, as shown by the values for mean deviation. Values for coefficients of variation, i.e. standard deviation, as a percentage of average coating, varied from 5·4 to 14·4 in lines 1 to 5. The mean coating values are less than for strip processed under similar conditions (after allowing for the two methods of expression); the value of 0·24 oz./sq. ft. of *surface* for Al/23 (line 8) may be compared with that of ¾ in. wide strip processed on the same occasion (Table VI, lines 12 to 14), which varied from 0·76 to 0·89 oz./sq ft. of *sheet*.

Structure and Bending Properties

The structure and bending properties of aluminised strip may be seen from Figs. 12*a*, 12*b* and 12*c*, showing the behaviour of narrow strip in a "close-bend" test, and Figs. 13*a*, 13*b*, 13*c* and 13*d*, showing the relationships between coating structure and bending properties of continuously aluminised wire.

Influence of Aluminising on the Physical Properties of the Steel Base—Combined Aluminising and Annealing

Reference has already been made to the fact that cold-drawn high tensile wire loses tensile strength when hot dip aluminised. This softening effect may be turned to good account by making it possible to omit an annealing operation when the product is expected to have physical properties approximating to those of the annealed

TABLE VII.—COATING THICKNESS ON CONTINUOUSLY ALUMINISED MILD STEEL WIRE.

No.	Ref.	Speed of Wire (ft./min.)	S.W.G.	Bath Composition	Temperature °C.	Sampled	No. of Samples	Coating Weight (oz./sq. ft. of surface)			Mean Deviation
								Mean	Max.	Min.	
1	Al/17 (Cu)	12·8	10	"Pure" Aluminium	740	Consecutive 6 in. lengths	10	1·18	1·36	1·06	0·09
2	Al/17 (G)	12·8	10	"Pure" Aluminium	740	Consecutive 6 in. lengths	10	1·41	1·58	1·24	0·055
3	Al/7	10	12	1½% Silicon	740 (?)	Consecutive 6 in. lengths	20	0·32	0·36	0·24	0·025
4	Al/10	10	12	2·65% Silicon	(?)	Alternate 6 in. lengths	13	0·35	0·39	0·31	0·018
5	Al/11	10	10	2·65% Silicon	(?)	Alternate 6 in. lengths	13	0·19	0·23	0·15	0·020
6	Al/11	10	12	2·65% Silicon		Consecutive 6 in. lengths	25	0·36	0·41	0·33	0·014
7	Al/12	10	12	2·65% Silicon	740	Alternate 6 in. lengths	13	0·28	0·33	0·20	0·031
8	Al/23	12	17	5·4% Silicon	740	Alternate 6 in. lengths	12	0·24	0·28	0·22	0·019
9	Al/27 (A)	25	16	6% Silicon	750	Alternate 12 in. lengths (A. and B at opposite ends)	6	0·27	0·28	0·26	0·003
10	Al/27 (B)	25	16	6% Silicon	750	Alternate 12 in. lengths (A and B at opposite ends)	6	0·20	0·23	0·17	0·018

condition. Mild steel strip, ¾ in. × 0·022 in., has been aluminised in the hard rolled condition with a fall in tensile strength from 40 tons/sq.in. to 28·6 tons/sq.in. (Fig. 22). Similarly, cold-drawn wire, 0·064 in. diam., on aluminising was reduced in tensile strength from 72·8 tons/sq.in. to 33·3 tons/sq. in. These materials were to be used as "strapping," and the physical properties were now approximately correct, the material being actually slightly too soft. This is easily remedied by modifying the time and temperature of immersion or by means of subsequent cold work on the coated product. This elimination of a separate batch annealing of strip or wire in coils is obviously of economic importance.

When thin strip is required of maximum ductility in the coated state, the slight hardening caused by rapid air cooling from above the eutectoid temperature is unwelcome. The effect can be reduced by controlled cooling.

Cold Working of Aluminised Strip and Wire

The appearance of the product is improved by cold rolling or drawing after coating. Coated wire drawn from 0·058 in. to 0·054 in. had an excellent lustre, and the alloy layer did not appear to have suffered any damage. Cold rolling in excess of 10—15% crushes the alloy layer in pure aluminium coatings; the impression gained by metallographic examination may be worse than the truth, for it is difficult to polish such specimens without losing some of the particles of alloy. This gives the appearance of gaps in the alloy due to the cold rolling.

With coatings high in silicon, it may be possible to draw down thick aluminised wire, and thus obtain a wire of the required gauge having the desired strength. The coating thickness will be reduced, of course, in the same proportion. The softening effect of aluminising may thus be overcome. This result has not yet been fully achieved, but the aluminised wire referred to above, when drawn to 0·054 in. had a tensile strength of 47 tons/sq. in. The basis steel contained in this case 0·30% carbon and 0·9/1·0% manganese.

Conclusions

The following discussion of the advantages and disadvantages of hot dip aluminised coatings, and of the coating process, is based on published information as well as on our own work. It is useful, in some cases, to make comparisons with hot dip galvanising; although each is likely to have its own field, such factors as the annealing action of aluminising or the relative danger of warping may decide the choice of process.

A.—Advantages of Hot Dip Aluminised Coatings

1. Aluminium is more resistant than zinc to normal atmospheric corrosion. The addition of silicon to commercial quality aluminium lowers its resistance to corrosion.
2. Its corrosion resistance is superior under those conditions which are bad for zinc, viz. sulphurous atmospheres or high humidity, or both together.
3. For a given coating thickness, the weight is less than half that of zinc. At present, with aluminium twice the price of zinc, there is about 20% economy in the cost of coating metal with aluminium. No allowance is made here for the relative amounts of iron in the two coatings. Aluminised coatings have been found to contain surprisingly high proportions of iron.
4. The future availability of aluminium may possibly be much more than that of zinc, so that the previous factor may have increasing significance.
5. The coating has useful heat resisting properties. If annealed to produce a completely alloyed coating for such applications, the hot dipped product behaves better than a sprayed aluminium coating during the annealing process. This is due to the continuous character of the steel, alloy and aluminium layers, which makes diffusion more uniform than across the steel/coating interface of a sprayed coating. In practice it should be easier to produce completely alloyed coatings from pure aluminium baths in one operation than to produce "galv-annealed" sheets.
6. A thinner coating is possible than in hot dip galvanising (without using aluminium). Using 5—6% silicon in the bath, a coating of 0·6—0·8 oz./sq. ft. of *sheet* may be applied to smooth strip without the necessity of using "skimming" or "exit" rolls.
7. Light cold rolling gives the product an excellent finish.

B.—Disadvantages of Hot Dip Aluminised Coatings

1. Owing to the presence of an inert, tenacious, and continuous oxide film, the electrochemical protection which would be expected from such an electro-negative metal is largely lost. The nature of the environment enters into this.
2. Arising from the above, a "pore" in the coating becomes more serious than a pore in a galvanised coating. The steel is anodic and pitting occurs. Cracks which form during deformation and which are regarded, in zinc coatings, as relatively harmless compared with much larger flakes, may be more serious in aluminised coatings.
3. The alloy layer is very hard and brittle when pure aluminium is used in the bath. Under compression, the coating fails badly, but under tension is better than hot dipped zinc. The presence of silicon in the bath improves matters, and other bath additions also are said to assist.

C.—Advantages of the Hot Dip Aluminising Process

1. Annealing and coating may be combined in one operation with obvious economic advantage.
2. The fact that exit rolls are not needed to produce thin coatings simplifies the process, as compared with galvanising, and reduces the amount of iron in contact with the bath (See also *D*9).
3. There is much less ash formation on a quiet bath.
4. Dross formation has some favourable aspects.
   (*a*) A given pick-up of iron leads to the formation of less dross due to the different composition —say 40% iron. One pound of iron leads to 16½ lb. of pure dross in galvanising, but only to 2½ lb. in aluminising.
   (*b*) Dross *should* settle more readily than in galvanising, for the difference in density between it and the bath (about 40% greater) is more than in galvanising (3%).

D.—Disadvantages of the Hot Dip Aluminising Process

The relatively high temperature of operation leads to most of the following disadvantages:—

1. More discomfort for the operator than in galvanising.
2. Fuel cost is greater.
3. Cold-worked high tensile material is almost completely annealed.
4. In mechanised processes for sheet and strip, the mechanical strength of the immersed "rig" is greatly reduced.
5. In continuous processing of thin strip or wire, excessive tension leads to marked thinning and even to rupture of the material while passing through the bath.
6. The dipping of fabricated articles, such as tanks or window frames, is likely to lead to more warping than is encountered in hot dip galvanising. Embrittlement due to ageing is less likely, however.
7. The best material for, and the probable life of, the container under industrial conditions may be a bigger problem than in galvanising.
8. The film of oxide on the surface of the bath can be a source of trouble by leading to an unsatisfactory appearance of the product.
9. When using silicon in the bath, the choice of coating thickness to be applied to smooth strip or wire is limited. The exit rolls used in sheet galvanising permit some control of coating thickness, according to the level of molten metal at the "nip." Aluminised coatings are thin enough without such rolls; to produce thicker coatings it would be necessary to specify a rougher steel surface finish.
10. Under certain conditions, the coating appears to have a tendency to de-wet, exposing the alloy layer and reducing the coating thickness to ½ mil or even less.

Acknowledgments

Valuable assistance with the design and construction of the pilot plant has been received from Mr. G. Popham (now of Esso Limited) and from Mr. Tom Rees, Engineering staff, Sketty Hall, who has also helped to operate the plant. Mr. R. H. Humphreys carried out the laboratory work on various types of fluxes, the micro-indentation testing of the alloy layer, and the metallographic work. Mr. Glan Thomas has assisted both in the operation of the process and with analytical and metallographic work.

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REFERENCES

1 E. J. Groom. *Sheet Metal Industries*, 1937, July, 611–613.
2 C. J. Fink. British Patent 415,732, U.S.A. Patent 2,082,622, (June, 1937).
3 Deligren, German Patent 632,993 (June, 1936).
4 Deligren, French Patent 743,843 (April, 1933).
5 Deligren, German Patent 634,135.
6 Nillson, German Patent 627,433.
7 Hoesch-koln Neussen A. G., German Patent 580,270.
8 H. Röhrig. "Hot-dipped Aluminium Coatings on Iron." *Zeitschrift für Metallkunde*, 1934, **26**.
9 K. Oganowski, N. W. Parks and K. G. Coburn, "Coating Ferrous Metals with Aluminium," U.S. Patent 2,406,245 (1946).
10 P. T. Stroup and G. A. Purdy. *Metal Progress*, 1950, Jan., **57**, 59.
11 D. O. Gittings, D. H. Rowland and J. O. Mack. *Trans. A.S.M.*, 1951, **XLIII**, 887.
12 M. Alferieff. Patent Specification 676, 198, Spain (Dec. 1, 1947).
13 M. Alferieff. *Comptes Rendus*, 1942, **215** (19) 433–435.
14 M. Alferieff. *Metaux*, 1945, May, **20** (237) 60–67.
15 J. C. Hudson. Corrosion Committee (Iron and Steel Institute) Protective Coatings Sub-Committee, February, 1946.
16 L. Guillet. *Le Genie Civil*, 1944, **64**, (13) 101, 103.
17 G. A. Möller. U.S. Patent, 2,315,725 (April 6, 1943).
18 A. Di. Guilio. *Light Metal Age*, 1948, June, 8.
19 C. G. Fink. U.S. Patent, 2,497,119 (February 14, 1950).
20 M. G. Whitfield and V. Sheahunoff. *Foundry*, 1951, Sept., **79**, 177–178, 180.
21 W. G. Patton. *Iron Age*, 1952, June 12, 115.
22 W. Hodge and E. M. Smith. *Materials and Methods*, 1951, Sept., 95.
23 *Proc. A.S.T.M.* 1944, **44**, 92–109. Report of Sub-Committee VIII on Field Tests of Metallic Coatings.
24 J. C. Hudson. Memorandum F5/46 to Corrosion Committee (Iron and Steel Institute) Atmospheric Corrosion Sub-Committee, March, 1946.
25 Post Office Engineering Dept. Research Report 12,420. Sept., 1947. "Examination of Aluminised Steel Sheet."
26 P. T. Gilbert—B.N.F.M.R.A. Memorandum 52. Nov., 1947. "Corrosion Tests on Armco Aluminised Steel."
27 B. P. Finkbone. A.S.M. Handbook (1948) 704.
28 J. C. Hudson and T. A. Banfield, *J.I.S.I.*, 1946, **CLIV**, 229.
29 Society of Automotive Engineers (U.S.A.) Aeronautical Material Specification AMS5036A. Issued January 4, 1943. Revised January 6, 1949.

More British Transformers For U.S. Dollars

THE Bonneville Power Administration has placed with English Electric Export and Trading Co., Ltd., a contract for a 250,000 kVA, three-phase transformer bank for service on the 230,000 volt transmission system in the State of Oregon. It will comprise three single-phase units, each unit, complete with oil, weighing 150 tons. The transformer bank will have auto-connected windings for a voltage ratio of 230,000/115,000 volts and a delta-connected tertiary winding for 13,200 volts will be included. On the 230,000 volt winding, on-load tap-changing equipment will be provided for a voltage range of 15%, and on the 115,000 volt winding there will be tappings for off-circuit operation for a range of 10%. Cooling equipment will incorporate airblast and forced oil circulation for the full output of 250,000 kVA. It will be adequate for an output of 150,000 kVA when the auxiliary cooling plant is idle. The transformer bank will be built at the Stafford Works of the English Electric Co., Ltd.

O.E.E.C. Cancels Copper Restrictions

COMPLETE cancellation of the common list of end-use prohibitions for copper and copper alloys, agreed upon by Member countries in September, 1951, has been decided upon by the Council of the Organisation for European Economic Co-operation: the new decision came into effect on 4th September, 1953. This common list was suspended in December, 1952, owing to the improved position of copper supplies, but the Organisation's Non-Ferrous Metals Committee was instructed to keep a close watch on the situation in case the re-imposition of restrictions became necessary. The Committee has now reported that the maintenance in abeyance of a common list of prohibitions serves no useful purpose, since the present satisfactory situation of world supplies has enabled all Member countries to remove their national end-use restrictions.

Contract Announcement

FRASER AND CHALMERS Engineering Works of The General Electric Co., Ltd., are to supply to the order of Guest Keen Baldwins Iron and Steel Co., Ltd. (Consulting Engineers, McLellan and Partners) one 5,000 kW turbo-alternator set, complete with condensing plant. This set is for an extension to the existing Power Station at their East Moors Works, Cardiff. The contract calls for one 5,000 kW direct-coupled pass-out condensing turbine running at 3,000 r.p.m. with inlet conditions 475 lb./sq. in. gauge with 750° F. total temperature, passing out 50,000 lb./hr. of steam at a pressure of 155 lb./sq. in. gauge. The vacuum will be 28·25 in., cooling water at 75° F. The G.E.C. alternator will be rated to give a 6,100 kW 10,500/11,500 volt, 3-phase, 50-cycle supply at 0·91 power factor under normal conditions.

Metal Casting Methods

VI—Die Casting and Investment Casting

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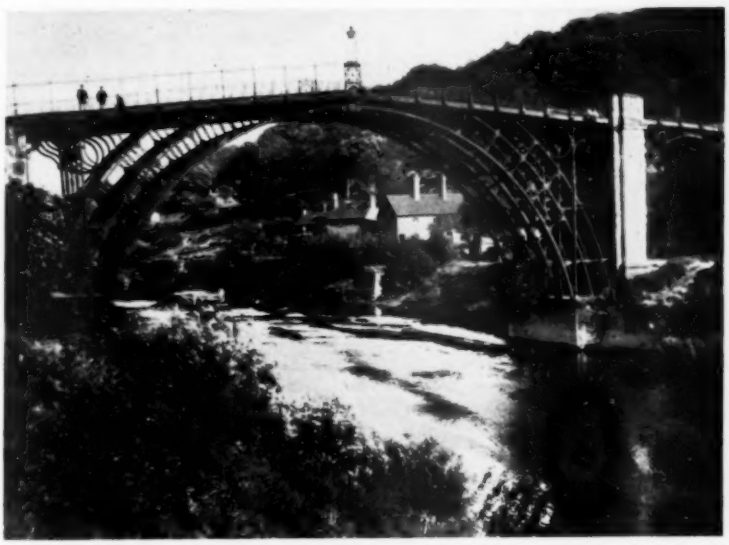
Continuing this series of articles on metal casting methods, the author begins an account of the methods of production of shaped castings by reference to the slush casting, press casting, pressure die casting, gravity die casting, and investment casting techniques.

SHAPED castings were produced for very many years before facilities existed for forging or other mechanical working. Stone moulds were used at first, and later clay or mud was used as a mould material. Readily smelted impure ores, such as those of lead, tin and copper, were used for the earliest castings known to us. A cast copper frog discovered in Mesopotamia is believed to be more than 3,000 years old, and many small tin bronze castings have been unearthed in China, including weapons and cooking utensils: the latter are thought to date from 1700 B.C. Bronze was then the principal casting material, though it is possible that cast iron was known to the Greeks before the sixth century B.C. The earliest cast iron object discovered in this country dates from A.D. 170. Bede mentioned cast iron in the early seventh century, though most of the early literature dealing with this material appeared in the Middle Ages.



The world's first cast iron bridge, erected 1779.

Metal casting was mainly devoted to the production of church bells, ornaments and ordnance. Golden bells were supposedly cast for the temple of Solomon, but the first record of a tower bell was that cast in Campania in Italy in A.D. 400. Church bells were imported into this country for more than 500 years, but British bell founding finally reached a high level of efficiency, and the craftsmen were highly esteemed. In York Minster, a stained glass window was installed in the year 1320, depicting the various stages of bell production, and it may be noted in passing that modern bell production technique shows little variation from that used a thousand years ago.

Old English stone mould (fourteenth century).

Cast bronze guns were made in the early fourteenth century, and were later replaced by the cast iron variety. The first cast iron cannon to be produced in England dates from 1509, and the Carron Company in Falkirk produced many cast iron guns in the early eighteenth century: these were widely known as Carronades. This firm of iron founders was established in the year 1759, and is still in business, though now concerned with light casting production. The cast iron bridge illustrated is still in existence, though now open only to pedestrians. It is believed to be the first cast iron bridge in the world, and was erected in 1779, spanning the river Severn at Coalbrookdale, Shropshire, England. This bridge has a span of 100 feet, and each semi-circular rib was cast in two pieces. Many such bridges were subsequently erected.

The advent of the printing press influenced foundry practice considerably, as the early wooden type was gradually replaced by the metal variety, and it appears that cast metal type was in use during the thirteenth century. On the decorative side, many beautiful ornaments and statues were produced by Cellini and his contemporaries, and the high standard reached by these workers has not since been exceeded.

Shaped Casting Production

Little fundamental difference exists between the production methods used for shaped castings and those used for ingots. In each case, the necessary outline is obtained by pouring molten metal or alloy into a previously prepared mould. Provision must always be made to combat the normal shrinkage occurring in cast material during the solidification process. The mechanism of solidification and shrinkage has already been discussed, and it should be noted that this involved process becomes extremely complicated in shaped casting production. Shaped castings are made when wrought material cannot be usefully or economically applied, and, since it is unusual for any mechanical work to be carried out on shaped castings, they must be of adequate soundness in the as-cast state. Foundry technique is, therefore, mainly based upon methods designed to obtain the maximum degree of internal soundness, combined with adequate surface finish and dimensional accuracy. Foundry production methods are at best a compromise, since the principal factors mentioned may not always be compatible with each other.

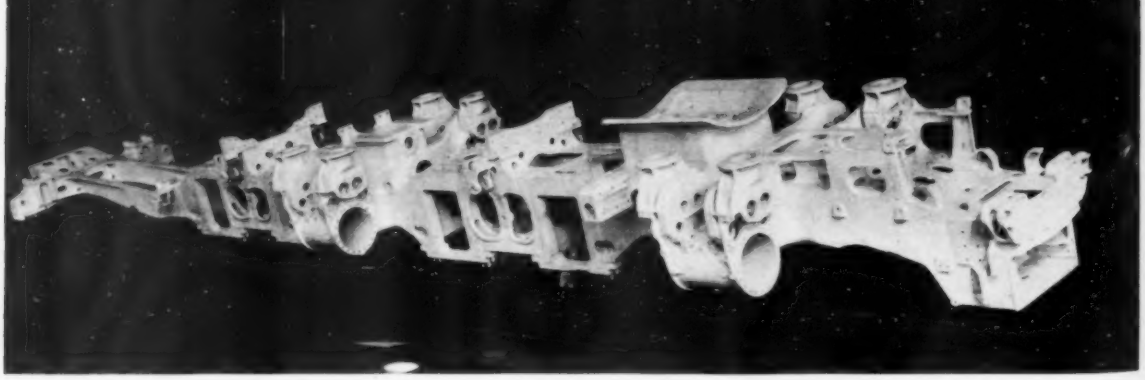
In the sand casting practice used to produce such shaped castings as those illustrated, intricate design is combined with a slow, and in many cases unpredictable, cooling rate. It will readily be seen that shaped castings present considerable technical difficulties in addition to those normally encountered in ingot production. Shaped castings may be produced in large or small numbers, depending upon the size of the order and the component required. Casting design and the type of alloy chosen are major factors, though subsidiary features such as application and cost also play an important part.

Few pure metals are produced in the form of shaped castings; this is mainly due to the poor physical properties of the common industrial metals in the as-cast state. Pure metals such as copper and aluminium are sometimes produced in sand cast form when components of high electrical or thermal conductivity are required. Most pure metals tend to be more liable to gas absorption than are their alloys, and this feature can have an appreciable effect on their application in the foundry. Gas absorption is reduced by the addition of alloying elements, and engineering castings are more often produced from alloyed material, the mechanical properties obtained being better than those of the pure metals. Cost is also an important factor.

The physical properties required in castings may be of an extremely varied character, and are generally dependent upon the application. The alloy chosen for a specific purpose must be assessed according to the main properties obtainable from that material. Strength, ductility, impact resistance, high strength to weight ratio, corrosion resistance and fatigue resistance may be required, depending upon service conditions. Mechanical strength is always valuable, and may be high, as in certain alloy steels, or comparatively low, as in certain non-ferrous materials. In all cases, strength should be adequate for the purpose, but high ductility values may not be essential in many castings. Castings intended for machine tools cannot readily be compared with those of a non-stressed nature, such as rainwater goods, while light alloy components for aircraft use are vastly different from those intended for more static applications. Corrosion resistance may be of paramount importance in certain instances. Many foundry alloys, notably cast iron, aluminium bronze and steel, are profoundly affected by the cooling rate after casting, and the variety of section thicknesses found in any typical casting will prevent an accurate assessment of the physical properties.

The main casting production methods are die casting and sand casting. The former includes all methods which use a static metal mould, while sand casting, as its name implies, is that portion of the field in which sand moulds are used. Considerable overlap exists in practice, as metal moulds may have sand inserts, and sand moulds are frequently made with metallic inserts. Theoretically, any casting may be produced by either method, but practical limitations are imposed by casting size and design.

Large castings are generally produced in sand moulds, since metal dies quickly become unwieldy if the casting weight exceeds a few pounds. Automobile radiator grilles are regularly made in die assemblies weighing several tons each, yet it is unusual to produce such large castings in metal moulds, and is only economical where very large orders of a continuous type are available. Very small castings, such as zip fastener units and core box vents, are produced as pressure die castings in this country and abroad. Very intricate castings are not

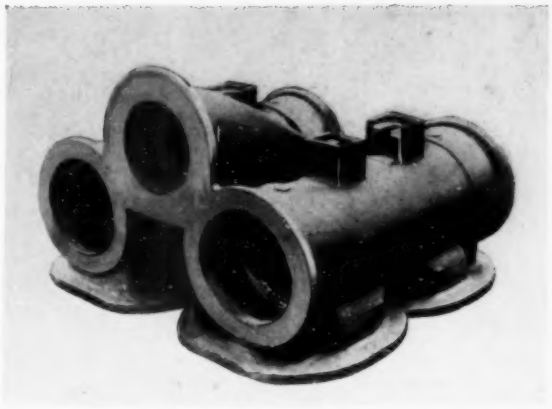


Courtesy of General Steel Castings Corporation, Illinois, U.S.A.

Nickel steel locomotive bed weighing approximately 33 tons.

produced by gravity methods in normal metal moulds unless sand cores are used ; if this is not possible, die cost is likely to be excessive, unless a large quantity of castings is required.

Die casting may be sub-divided into the following groups. (1) slush casting, (2) press casting, (3) pressure die casting, and (4) gravity die casting.



Courtesy of J. Stone & Co., Ltd.

Leaded gun metal pump casting weighing 30 cwt.

Courtesy of Sterling Metals, Ltd.

Aircraft nosewheel leg casting made in Z5Z magnesium alloy and weighing 40 lb.

Slush Casting

The slush casting technique is extremely old, and slush cast articles have been discovered during excavations in Egypt. This process is used extensively in the production of small articles of an ornamental or otherwise non-stressed character. Toy soldiers are usually produced by slush casting methods, and aluminium kettle spouts are made in the same way. A slush casting is a hollow casting formed in a static metal mould without the use of cores. The mould is filled with molten metal, and after a suitable interval has elapsed the bulk of still liquid material is poured out. A thin-walled casting is thus produced with minimum metal consumption.

Large steel rolls for hot working purposes have occasionally been produced by a modified slush casting technique. Sand moulds of normal design were filled with liquid alloy steel, and when a skin of reasonable thickness had been formed on the inner mould faces, the remaining liquid material was drained into a ladle. In this way, valuable alloy steel was recovered, and the hollow roll interior was then filled with cheaper grey cast iron to make a solid casting. Small articles may readily be slush cast by a simple mould inversion technique, while larger components are more easily made if the excess metal is allowed to drain from a hole provided near the base of the casting.

Press Casting

Press casting is sometimes known as the Cothias process, and is similar to that already described for the production of copper ingot moulds. A measured amount of liquid metal or alloy is poured into a shaped mould, and a metal core mounted on a plunger is forced into the molten material. A hollow casting of the required internal and external shape is thereby produced. The product is excellent, though pressed castings are of rather limited size and design. Sokolov described a new method of stamping shaped articles from molten alloys, while the Bacco process described by Du Mond is of a similar nature. Some advantage is claimed in both cases if the metal die is heated while pressure is applied to the contents.

Die Casting

Gravity and pressure die casting are similar in many respects to each other. In the first case, gravity is the only force applied to direct the molten alloy into the mould cavity. Pressure die casting, as the name suggests, involves a feeding device, in which pressure is mechanically applied, either by compressed air or by means of a piston. Many small castings may be produced by either the gravity or the pressure methods; the controlling factors are the size of the casting, and the number of such castings which are likely to be required. The type of alloy under consideration and the accuracy needed are also important. Medium sized castings are usually produced by gravity die casting only and orders of less than 500 castings are not normally considered for production by this method, although much depends on the casting design, and on the prospect of future orders. If expensive machining operations can be reduced or eliminated, pressure die casting may be adopted, even though only a relatively small number of castings are needed. Generally speaking, quantities of less than 5,000 are not economically produced as pressure die castings. Any ferrous or non-ferrous alloy may be gravity die cast, though non-ferrous alloys are more commonly produced in this way. Steel die castings have been made, but the high working temperatures needed have prevented the general application of this system. The metallurgical difficulties concerned are less important.

A very large tonnage of grey cast iron is produced in the sand cast form, but grey iron die castings have been made since 1908. Cast iron practice shells were die cast during World War I, and the system was subsequently applied to a variety of commercial castings. Two processes have become established for iron die casting in gravity moulds ; they are the Holley and the Eaton-Erb processes respectively. Minor differences exist, though the plant used is essentially similar in both cases.

The process was originally carried out with manually-operated lever-type, single-head machines. A cam-operated turntable was later introduced, and, finally, a 12-head, semi-automatic, air-operated machine with rotating moulds and suction cooling was adopted. Each

machine consists of a large base upon which revolves a duodecagonal hub. Twelve hollow arms are bolted to the hub, extending radially, and an outer head, bearing a half mould, is attached to each arm. The outer heads are partially hollow, and 500 cu. ft./min. of air are drawn across the back of the mould, through the head, and pass finally through the radial arms into the hub. Twelve inner or moving heads are mounted on rollers, and movement is obtained by means of 8 air cylinders which are valve-operated to close, open, and hold the moulds. The inner head in each case is air cooled by a telescopic attachment. A cam-operated device controls the mould dressing system, which is simply an acetylene flame depositing a carbon coating on the mould faces. The same mechanism actuates the jet of compressed air which removes loose dirt from the mould halves.

The whole assembly is rotated by an electrically driven gear unit, and speeds varying from one revolution in two minutes to one revolution in six minutes may be used, depending upon the size of the castings produced. A maximum mould temperature of 150°–250° C. is maintained and the pouring temperature is between 1260° C. and 1320° C., depending upon the casting size. Iron die castings show undercooled graphite in the microstructure, and very thin sections may be chilled to some extent : all castings are subjected to an annealing treatment. Castings up to 30 lb. in weight have been produced by this method. Die life is variable, tending to decrease as the intricacy of the casting design increases. Fairly intricate dies have been used 35,000 times before failure.

Pressure Die Casting

Modern pressure die casting technique has been developed from the first type casting machine, which was invented in the U.S.A. by Sturgis in 1849. In this machine, the liquid metal supply was pressure-fed into the mould cavity by means of a lever and plunger arrangement. In 1877, Dusenbury adapted this principle to the production of white metal bearings, and Mergenthaler, in 1885, developed the linotype casting machine which has since been widely used. A pressure die casting machine operated by compressed air was introduced by Van Wagner in 1907.

Modern type casting machines are simply die casting units of a specialised nature. Type casting machines may be considered in two groups :

(1) monotype machines, which cast individual type units, and
(2) linotype machines, which produce a complete line of type as a single casting.

In the monotype machine, a lettered and numbered keyboard unit is operated in typewriter fashion, producing a series of punched holes in a moving roll of paper. The latter is then transferred to the casting machine, and slowly unrolled. As the perforations are exposed, compressed air is forced through them, in order to bring the correct matrices into position. The latter are simply engraved metal strips bearing the impression required, and are drawn into position at the end of the mould. Liquid alloy is then pumped into the mould, producing a single figure or letter. The casting is then trimmed to standard length, and automatically transferred to the waiting tray. Type produced on monotype machines is very sharp in outline, since individual casting is the rule, and rapid solidification is obtained. A lead-base alloy containing 8% of tin, and 15% of antimony is used.

The linotype machine is also provided with a keyboard, and as the keys are operated, brass matrices are assembled in front of the mould, and molten alloy is pumped in. A slug or casting of " line-of-type " is then produced, which bears the required lettering and numbering on one end. The casting is then ejected, and trimmed to size. Rapid solidification is essential, and a lead-base alloy containing 3% of tin and 10% of antimony is used for this work. Linotype is remelted and cast before use, while monotype can be re-assembled, unless its useful life has been exceeded. The whole series of printing metals lies in the range 2–20% tin ; 10–30% antimony ; and the remainder lead.

Early pressure die casting was restricted to lead- and tin-base alloys, which were comparatively easily handled. The introduction of zinc-base and aluminium-base alloys necessitated some modifications in machine design, particularly in the valve mechanism.

Pressure Die Casting Machines

Pressure die casting machines are of varied designs, but three main features are common to all.

(1) The pump or pressure device, in which molten metal is subjected to pressure at intervals as the die is filled.
(2) The frame for opening and closing the die halves.
(3) The locating device which holds the frame and die assembly against the pressure chamber.

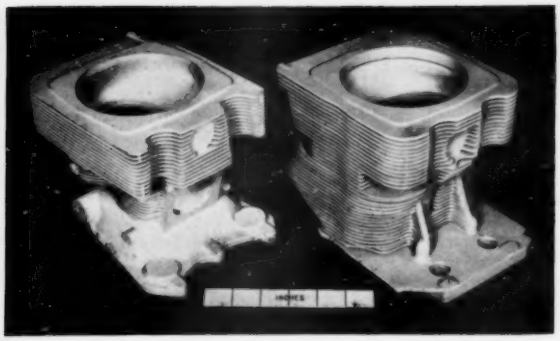
The pressure chamber in the plunger type machine consists of a submerged cylinder containing a plunger or piston. A forward stroke of the plunger forces molten alloy into the die cavity through a suitable nozzle. On the return stroke, a side port opens, allowing more liquid alloy to enter the cylinder by gravity feed from the surrounding pot. In the pneumatic-type machine, air is applied directly to the metal surface. The pressure chamber, known as the " gooseneck " owing to its shape, is filled by submersion in the melting pot, after each casting is made. The gooseneck is then locked against the nozzle seat of the die, and a valve mechanism is operated ; molten alloy is thereby forced into the die cavity by air pressure. After a short time has elapsed, the die assembly is opened, and the casting ejected.

Both the plunger and pneumatic machines described are of the hot chamber type. The Polak cold chamber machine was devised to avoid the limitations imposed by the hot chamber method. Cold chamber units were first used for brass, and were later adapted for aluminium, magnesium and zinc alloys. In these units, the molten metal is ladled from a separate crucible into a cylinder, where it is supported on a spring-loaded piston. No liquid metal is allowed to come into contact with the runner. A plunger is then depressed on the liquid metal, and the piston beneath is forced down. The metal supply is then allowed to pass into the runner, and hence into the die cavity. As the plunger is withdrawn, the spring loaded piston returns to its original position, thereby shearing off the runner and ejecting a disc of surplus metal.

Pressure die castings can be produced at a very high rate, and 500 ' shots ' per hour is not unusual in small automatic machines. Much will depend upon the type of castings produced, and upon the pressure applied. The latter may range from 50 lb./sq. in. to several tons, depending upon the type of casting unit used. A pressure die is usually made in halves, one of which is fixed, and the other capable of movement. Each die may be of the single type, or of multiple cavity design.

Courtesy of High Duty Alloys, Ltd.

Large pressure die casting machine.



Courtesy of Sterling Metals, Ltd.

Cylinder head castings die cast in " Y " alloy.

Single dies are relatively cheap to make, and are used for small orders where die cost must be limited. Multiple dies contain more than one impression of any component. So-called combination dies are sometimes made, in which several impressions of various components are arranged. Combination dies are useful when a group of castings of various shapes and sizes is required for subsequent assembly into a single component. Accurate disposition of each cavity is essential if a balanced solidification rate is to be obtained.

Pressure dies are generally designed so that the major part of the casting tends to grip the movable half die. When the latter is withdrawn, suitably disposed ejector pins lift the casting off the die face. Chrome-vanadium steels are often used for zinc-base and aluminium-base alloys, while brasses are cast in dies made from tungsten-chromium steels, which retain much of their original hardness at red heat. Whenever possible, dies for pressure work are machined in the soft state, checked dimensionally by a few trial shots, and then fully hardened before going into service. Die life is profoundly affected by the working temperature : steel dies used for zinc-base work may last up to 500,000 shots, yet a life of 50,000 shots would be more likely if aluminium alloys were cast, and brass would reduce the life of a similar die to approximately 500 shots. Cores and loose pieces may have a shorter life than the main die, if the former are unduly exposed to elevated temperature or wear.

Pressure die casting is mainly confined to non-ferrous alloys, though some " vacuum casting " has been carried out on grey cast iron. A limited amount of low pressure die casting is carried out in England, using grey cast iron moulds and working pressures less than 50 lb/sq. in.

Gravity Die Casting

Gravity die casting or permanent moulding, is used for the production of shaped castings in a more convenient or economical manner than is possible by the alternative methods which are available. Metallic dies are generally used, though refractory dies have found some application. An outstanding advantage of the die casting process is that comparatively unskilled labour may be used for casting production, while highly skilled labour is utilised to greater advantage for die manufacture. Gravity and pressure die casting systems are essentially mass production methods which are used for the production of relatively large numbers of identical castings ; neither gravity nor pressure dies can be readily modified if the original die design proves inefficient.

Castings produced in gravity dies have better surfaces than similar castings which have been produced in sand moulds, and the greater solidification rate obtained in die casting promotes pressure tightness in the castings, which are usually produced to closer limits than is usual in sand cast products. The aluminium alloy cylinder head casting illustrated has been regularly produced in gravity dies. The fins are of only 4 mm. pitch, and it is unlikely that such dimensional accuracy could be obtained from a sand casting.

Low production costs are the most attractive feature of gravity die castings ; the remaining advantages being minor considerations. Pressure die castings, on the other hand, may be specified for a particular application, where it may be desirable to obtain castings requiring little or no machining, and having many thin sections.

Casting size and design will exert a controlling influence on the die casting method used, and the following main points should be considered before any method is adopted. Section thicknesses should be equal, as far as is possible, and section changes should be blended smoothly into each other. A general minimum section thickness is $\frac{3}{16}$ in., though castings of $\frac{1}{16}$ in. thickness may be produced ; much will depend upon the total surface area of the casting under consideration. Small castings of thin section are more easily produced than larger components. Large flat areas are especially difficult to make, and some camber is usually introduced. Reinforcing ribs should be 50% thicker than the supporting section, and generous fillets should be provided between ribs and other sections.

Taper is normally provided in all shaped castings, and is particularly important in gravity die castings. During solidification, the casting tends to shrink away from the outer mould faces, and to contract tightly around the inner surfaces : more taper is, therefore, needed in the latter case. The amount of taper used is variable, but may range from 1° to 3° on outer surfaces, and up to 5° on inner surfaces. In all types of casting, production is facilitated if the mould parting or joint lines are straight, though this is not always possible. Undercut portions are difficult to die cast without the use of cores, or of multi-part moulds. Multiple cores and long thin cores should be avoided, unless they are piloted into the opposite die section. In normal die casting technique,

metal cores are withdrawn before the casting is extracted from the mould : interlocking cores are not recommended. It is useful to arrange core movement to be in the same direction as that of the die ; cores may then be attached to one die half.

Die Design

The die blocks used in gravity work are usually of grey cast iron, and are not subjected to any heat treatment in normal practice. Little advantage has been gained, for normal work, by the use of more expensive die materials. Each die part is arranged so that an average mould wall thickness of three to four times that of the component wall thickness is obtained. Excessive die wall thickness should be avoided, in order to prevent unequal contraction occurring, with the possibility of cracked or warped castings. A reasonable temperature balance can be obtained if the rear of each die block part is machined to the appropriate thickness. Controlled heat transfer can also be obtained by judicious applications of die dressing, where a reduced cooling rate is required.

Most gravity moulds are of the two-part type, and are manually operated. It is useful to mount the die halves on a suitable base plate in order to facilitate rapid movement, and correct location is easily obtained by steel dowels attached to one half, mating with holes in the opposite half. Elaborate ejection equipment should not be required in gravity die casting, and simple ejector or knock-off pins are generally used.

An automatic machine for gravity die casting aluminium alloys has been described by Bourret, in which all the individual operations normally carried out manually are mechanised. The machine consists of a metal frame on which is mounted a circular base plate. The gravity die is mounted on the base plate, and may readily be filled by tilting the latter to a predetermined angle. A number of cylinders and piston assemblies are attached to the periphery of the base plate, and are used to provide for horizontal or oblique die motion. Core removal is carried out by means of another cylinder and piston assembly operating in a vertical direction. Die opening, closing and tilting are all mechanised, as are die coating and cleaning : the only manual operation is the pouring in of the metal. Such methods would appear to be very useful, but are not supported by the general belief that gravity die casting systems must be essentially simple if they are to be economic.

Alloys Used

Alloys used in die casting cover a very wide range. Any commercial alloy may be die cast, provided that sufficient care is taken in die preparation. High temperature alloys are not so easily handled as the more conventional zinc-base, tin-base, lead-base, aluminium-base and magnesium-base alloys. Copper-zinc and copper-aluminium alloys fall into an intermediate category. Lead and tin-base alloys were originally used to a large extent for die castings, but are now only used where extreme accuracy and high corrosion resistance are required. An alloy of 70% tin and 30% antimony is used for the covers and grids of gas meters, and alloys of 90% tin, 5% copper, 5% antimony and 85% lead, 10% antimony and 5% tin may be used for certain optical parts.

More than 90% of all pressure die castings are made in zinc-base alloys of the Mazak type. There are several Mazak alloys, each having an aluminium content of 4%, and containing small amounts of magnesium. The principal difference between the grades lies in the copper content. Zinc-base alloys are invariably made from high purity zinc, and the ease with which they may be melted and cast has led to their use in electrical, household, and a variety of industrial applications. A large proportion of zinc-base die castings are electroplated before use.

Aluminium and magnesium alloys may be gravity or pressure die cast, but magnesium alloys are extremely reactive, and pressure die casting has only recently become a commercial proposition. Similarly, the high-strength aluminium-base alloy containing 10% of magnesium was not easily made in die cast form until comparatively recently. Alloys of high fluidity, such as the Alpax series, are especially suited to pressure die casting, while the other aluminium alloys are more frequently encountered in the gravity die cast state, but with the development of high pressure, cold chamber machines, any aluminium alloy may be pressure die cast.

A limited amount of brass gravity die casting is carried out, but the demand for such articles is limited : nor is pressure die casting widely applied to brasses. Appreciable quantities of aluminium bronze castings are produced in the gravity die cast form, and many small engineering components which are liable to abrasion and corrosion in service may be readily produced in this way.

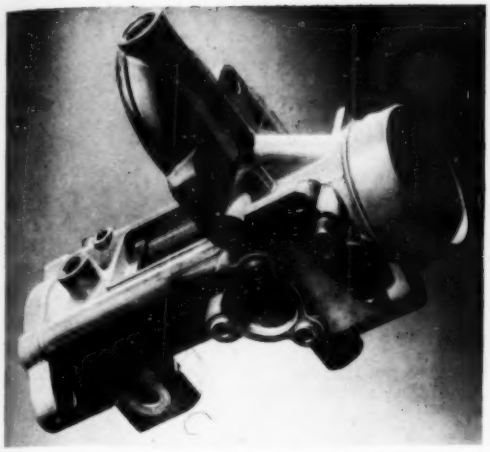
Pressure die castings which have been made in modern cold chamber, high pressure machines are less liable to internal porosity than are those castings made in hot chamber units operating at lower pressures. In the cold chamber process, the high working pressure forces the molten alloy into the die cavity, and an increased cooling rate is obtained owing to the enforced contact with the metal mould. Some porosity is still likely to be found, however, since liquid alloy is forced into the vents when the die is filled. Most of the air contained in the mould is expelled before the vents are sealed, yet a proportion of this air is trapped in the casting.

Gravity die castings are less liable to suffer from such defects. Other defects may be encountered in the gravity die cast product, though these are mainly of a metallurgical character.

Mould material is a common source of defective castings in sand foundry practice, and Murphy has shown that aluminium bronzes are less liable to surface defects when die cast than when produced in the sand cast state. This is equally true when other alloys are considered, and if a metallic mould material is used, many foundry difficulties can be avoided.

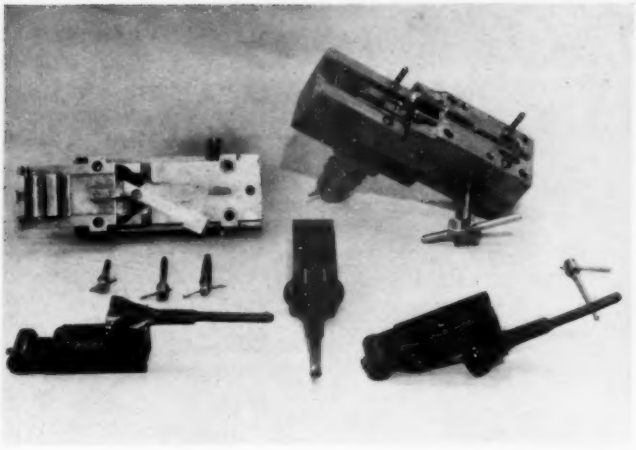
Investment Casting

This casting production technique is often described as the " lost wax," or " precision casting " method. since these titles were thought to indicate the special features of a process in which wax patterns made to close dimensional limits were coated or invested with refractory material : the assembly being stoved subsequently to remove the wax, and then cast. Alternative pattern materials, such as frozen mercury and low melting point resins, have been developed, and the introduction of improved mould materials has facilitated the production of castings to close limits. " Investment casting " is a more appropriate term, since it indicates the special technique which remains a characteristic feature of the process. " Investment " in this case is



Courtesy of The Zinc Alloy Die Casters Association

Carburetter body die cast in zinc-base alloy.



Courtesy of Machinery

Metal mould assembly for wax patterns of shot gun body, with three patterns in the foreground.

used in the same sense as the term "enrobing," is applied to the production of chocolate-coated sweets.

It is well known that the original lost wax techniques are many hundreds of years old, but the investment casting methods now used have taken less than 20 years to find industrial application. Large scale industrial work in this field was originally carried out in order to produce turbine blading for aircraft, when precision machining facilities were extremely limited. Some of the alloys used were extremely difficult, if not impossible to machine, and hence metallurgical developments stimulated work in the field of castings production. There are many components in the engineering field which are of such intricate design that normal production methods are both time-consuming and expensive. Certain parts for small arms, sewing machines, and spinning machines are of this type, and milling cutters can also be included in this category. The techniques involved in the production of such castings are similar to those first used for turbine blades.

In engineering practice, it has been found that any alloy which can be cast into shape by normal methods can also be processed by investment casting. Sillimanite was originally chosen as the best moulding material for investment castings, and remains popular in this field. Zircon sand is used for nickel-rich alloys, since the latter are reactive at normal casting temperatures. Silicon carbide finds application where a mould material of relatively high thermal conductivity is required, but the tendency of this material to react with ferrous alloys limits its wider application. A stable form of silica, which is mainly cristobalite, is now finding some application as an investment moulding material. The first bonding agent to find general application was ethyl silicate, and, despite the high cost of this material, no suitable alternative has yet appeared.

Mould materials for wax patterns include lead-base white metal and a mixture of sulphur and graphite. Flexible moulds of the rubber or polyvinyl chloride type find less application. Patterns for engineering components of complex design normally require complicated moulds, similar to those in use for pressure die casting. A typical metal mould designed to produce wax patterns for a shot gun body is illustrated. Three such patterns appear in the foreground.

The following description indicates typical British practice in the investment casting field. A master pattern is used to prepare a plaster oddside, and the latter used in turn to prepare a metal half-mould. A second metal mould part is then made to match. A limited amount of finishing is usually needed to ensure dimensional accuracy. Silicone mould release agents are then applied to the mould parts to facilitate stripping. Wax is injected into the metal mould assembly under controlled conditions, time, temperature and pressure being important in wax pattern production.

After stripping, the wax patterns are cleaned and checked dimensionally. The appropriate number of patterns are assembled together into a cluster by means of a heated spatula, and the cluster is then given the first investment, either by dipping or spraying with a sillimanite-ethyl silicate slurry. When the primary investment operation is completed, the assembled wax clusters are dried slowly, and then inverted prior to fusion on shallow steel trays. The primary investment is extended to the base of the pattern assembly and the supporting trays. A tapered metal box is placed on the tray, and filled with the final investment mixture. The filled mould is then vibrated to consolidate the refractory mixture around the wax pattern assembly. Drying and wax reclamation occupies about 36 hours, and is carried out by stoving the inverted moulds at 90° C. The dried moulds are afterwards stripped and slowly raised to 1050° C. to stabilise the bonding material.

Casting is normally carried out under gravity, but some centrifugal casting is also practised. Typical castings produced in this way are illustrated, and it should be noted that it may often be economic to carry out a limited amount of machining if necessary.

REFERENCES

1 Barclay. *J. Inst. Met.*, 1932, **49**, 230.
2 Genders and Bailey. "Casting of Brass Ingots," 1938. 12. 114.
3 Junker. *Z.f. Metall.*, 1926, **18**, 312.
4 Cook and Fletcher. *J. Inst. Met.*, 1949 (Jan.), 353.
5 Hessenbruch and Bottenberg. *K.W. Inst. f. Eisenforschung*, 1931, **13**, 205.
6 Oertel. *Stahl und Eisen*, 1929, **49**, 696.
7 Erichsen. B.P. 358,697; 299, 850 (1929); *Metal Industry*, 1938, **53**, 251.
8 Simpson. "History of the Castings Industry," 1949.
9 Schubert. *J. Iron and Steel Inst.*, 1942, II, 151 P.
10 Sokolov. *Engineers Digest*, 1948, **9**.
11 Du Mond. *Materials and Methods*, November, 1949.
12 Custer. *Trans. A.F.A.*, 1917, **26**.
13 Holley. B.P. 199,390. (1924).
14 Erb and Bremer. *Foundry*, 1933 (June).
15 Pollard, Redshaw and Payne. I.B.F. 1946–47. A30.
16 Stern. *Diecasting Practice*. 1930, **8**, 161.
17 Dusenbury. U.S.P. 189,090.

Fractographic Patterns of Segregation*

By Carl A. Zapffe, M.S., Sc.D.
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The work of Dr. Zapffe on the examination of fractured surfaces, by the special microscopic technique which he developed, is well known to metallurgists. In this article, he describes some interesting constitutional features that have been observed as variations of fracture traverse caused by segregation.

WHEN solids fracture, the path of the separation produces a pattern which has been used for centuries, on a macroscopic scale, for determination of the quality of metal, and as a general control of metallurgical processes. Only in recent years has it been found that fracture patterns are even more informative on a microscopic scale. During World War II, problems of fracture attained particular importance, a well-known instance being the failure of welded ship structures. About this time, the author developed a special microscopic technique which allowed examination of minute fracture structures visible at high magnification on fresh and untouched fracture surfaces. The technique was first described in 1943 in T.P.1553 of the American Institute of Mining and Metallurgical Engineers in the course of a study of hydrogen embrittlement, and was presented in 1945 to the American Society of Metals[1] as a new research tool for the general study of fractures. Two papers appeared in the *Journal of the Iron and Steel Institute* in 1946 detailing some findings principally of theoretical interest ; and later applications were shown also to have some practical value, as in the production of cast molybdenum, the study of ship plate, and the determination of a fatigue condition in metals. Fractography is the name now given to the descriptive treatment of fracture.

Two general classifications of fracture pattern are recognised. The first is the *endogenous* pattern, so-called because dehesion during fracture follows paths of weakness pre-existing in the solid. The second is the *exogenous* pattern expressing transient configurations of the rupturing force, without deflection from inherent weaknesses of the matrix. This Type II pattern is a characteristic of fractures in amorphous bodies, such as glass and obsidian, where directionalism neither develops from crystallographic features nor from imperfections in crystal growth.

On the other hand, Type I patterns display both the

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Fig. 1.—Fractograph of a zinc alloy containing approximately 10% aluminium, showing a eutectic structure with excess β-phase. Fine trigonal markings within the bright phase designate this as a basal cleavage in zinc-rich *beta*. × 300

Fig. 2.—The same specimen as Fig. 1 polished and etched with CrO_3-Na_2 SO_4 solution, confirming the fractographic description. × 300

directionalisms of crystallography and of imperfection ; and these accordingly become of the most interest to students of the solid state. The following discussion calls attention to several of a great number of peculiarities that have been observed in fractographic patterns of alloy systems where segregation has affected crystal growth. Two varieties of segregation will be considered : (1) a separation of phases in an immiscible system ; and (2) a compositional variation in a miscible system.

Zinc-Aluminium

In Fig. 1 a fractograph is shown for an alloy of zinc with approximately 10% aluminium. The zinc-aluminium binary system has a eutectic near 5% aluminium, combining a hexagonal-close-packed β-phase of nearly pure zinc with a face-centred-cubic γ-phase rich in aluminium. A eutectiform structure appears in this pattern ; furthermore, close observation of the bright phase discloses faint trigonal symmetry virtually identifying this as zinc-rich *beta*—probably $\{10\bar{1}2\}$ twinningex pressing itself upon a (0001) basal facet.

In Fig. 2, a conventionally polished and etched sample confirms these identifications and provides an unusually instructive instance of the similarity of fractographic and metallographic patterns. The etchant shows that the large pockets and the black gridwork within the eutectic area are γ-phase. While these dark areas of Fig. 2 result from preferential etching, the closely corresponding pattern of Fig. 1 follows from an unfavourable fractographic characteristic common to aluminium and its alloys[2]. The easy cleavage of zinc leads to a development of photographable facets, but the fracture of aluminium is extremely uneven.

Bismuth-Antimony

Segregation of a more subtle type is illustrated in Fig. 3. Here a specimen of bismuth containing 1·7% antimony displays a basal (0001) cleavage within a single grain of a cast polycrystalline sample fractured by impact. The broad grey bands are $\{10\bar{1}4\}$ twins expressing plastic deformation prior to fracture. In pure bismuth these are always remarkably straight, and of fairly even width. The present deviations in both direction and width undoubtedly refer to

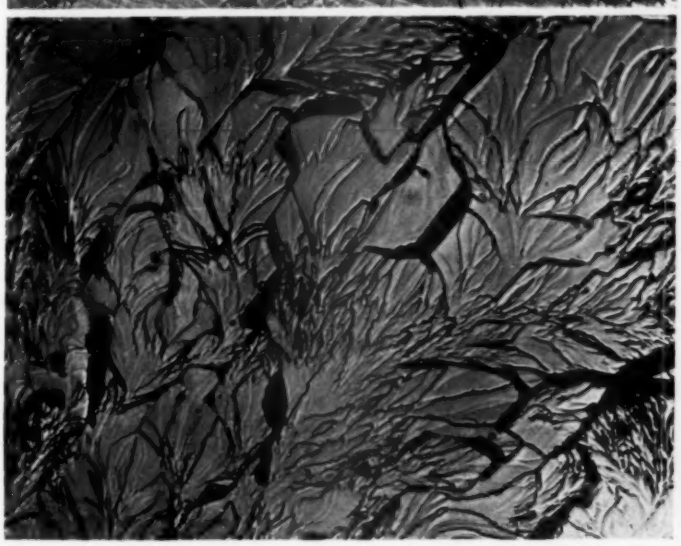

Fig. 3. (Top)—Basal cleavage in cast bismuth containing 1·7% antimony, showing broad twin bands and other endogenous markings strongly distorted by segregation effects. × 330

Fig. 4. (Middle)—Basal pattern similar to Fig. 3, but showing pronounced distortion of the wavelike markings in conjunction with twin bands which have acted in both deformation and fracture. × 45

Fig. 5. (Bottom)—Basal cleavage in bismuth containing 10% antimony, showing a multiplicity of fanlike fracture units characteristic of the central compositions in this system. × 400

Fig. 6.—Segregation effects on a secondary cleavage facet of antimony containing 46% bismuth. × 175

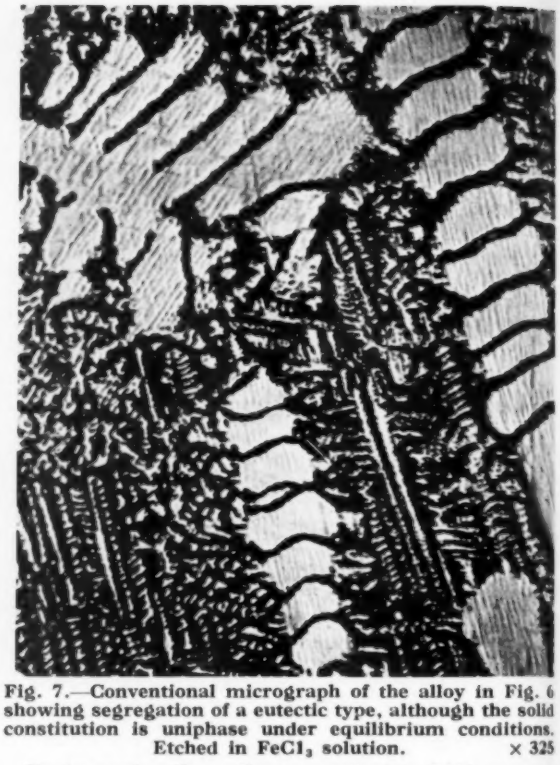

Fig. 7.—Conventional micrograph of the alloy in Fig. 6 showing segregation of a eutectic type, although the solid constitution is uniphase under equilibrium conditions. Etched in $FeCl_3$ solution. × 325

distortion and imperfection developing during growth of the crystal, due, in turn, to the antimony content. The bismuth-antimony systemis a single solid solution ; nevertheless, the temperature range between liquidus and solidus is unusually wide, often producing segregation effects as marked as those of a 2-phase system.

As for the wavelike pattern, this is particularly interesting. In the first place, these markings are almost entirely *endogenous*, expressing some feature of the crystal, rather than the exogenous fracture fronts which they so strongly resemble. They are the " rifflemarks " referred to in a previous paper[3], and they commonly display indices of the form $\{11\bar{2}c\}$, hence disposed 30° to $\{10\bar{1}4\}$ twins. The symmetry can be seen in Fig. 3, and more clearly in Fig. 4, if one neglects the distortion. Annealing brings these markings into geometric position, which proves their endogenous nature. Furthermore, their inter-relationships with other fracture configurations show that they represent a crystallographic weakness having the nature of a secondary cleavage[3]. They may represent growth discontinuities—although this has not been proved—but their distortion in Figs. 3 and 4 strongly suggests a structural influence of the antimony content.

In Fig. 5, an alloy of bismuth containing 10% antimony introduces a further variation in fracture traverse. The facet is again basal, but it is now overlain with a great number of branching fracture individuals, usually to the complete exclusion of observable twinning in this composition range. These tearline groups may in themselves constitute exogenous patterns[4], but the fact of their repeated presence has an endogenous aspect, since the pattern of Fig. 5 is distinctive for the intermediate bismuth-antimony alloys.

By increasing the antimony content to 54% segregation in the cast alloys approaches a maximum. Basal facets remain similar in appearance to that of Fig. 5, though the leaf-like forms are more numerous. Occasionally the individual crystal fractures on secondary cleavage families. A new pattern of segregation then appears, again strongly marked and characteristic, as shown in Fig. 6.

For these intermediate compositions, secondary cleavage more or less evenly divides itself between the rhombic $\{10\bar{1}1\}$ form common to bismuth and the $\{10\bar{1}4\}$ form common to antimony. Since the latter is also the twinning family for both metals, fracture sometimes displays the phenomenon known as " parting "[5]. Either type of secondary facet shows a regular and geometric pattern for the pure metals, but variegated for the unannealed alloys as shown in Fig. 6. The horizontal markings in that fractograph are intersecting basal planes : the spaced flats in the fracture traverse express segregation effects, which are clearly depicted in the conventional micrograph of Fig. 7. The segregation is seen to be about as pronounced as that of a 2-phase system, and it is not surprising that a great deal of discussion has centred upon this otherwise simple constitution[6].

REFERENCES

1 " Fractography—A New Tool for Metallurgical Research." C.A. Zapffe and M. Clogg, Jr., *Trans. Amer. Soc. Metals*, **34**, 71–97 ; disc. 98–107 (1945).
2 Studio Frattografico Delle Leghe Zn-Al Ad Alto Tenore di Zinco." C. A. Zapffe, C. C. Worden, and F. K. Landgraf, *Metallurgia Italiana*, **43**, (3–4), 97-109 (1951).
3 " Fractographic Structures in Bismuth," C. A. Zapffe, *Metal Prog.*, **50**, (2), 283–6 (1946).
4 " Metal Fractures Modeled by other Materials," A. M. Sullivan and J. A. Keis, *J. Metals*, **188**, 1090–1 (1950).
5 Fractocristallographie—Methode d' Identification des Caracteristiques Cristallographiques de Deformation et de Fracture Dans les Solides Polycristallins," C. A. Zapffe and F. K. Landgraf, *Rev. de Metallurgie*, **48**, (11), 811–21 (1951).
6 " Der Aufbau der Zweistoffiegierungen," M. Hansen, J. Springer, Berlin, 1,10[illegible] pp. (1936).

Carbon in the Engineering and Metallurgical Industries

II—Industrial Carbons

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In the second article of the series, the author discusses the industrial carbons and their uses. Details are given of the raw materials from which they are made, and of the processes used in their production. Finally, reference is made to typical applications in selected industries

RAW MATERIALS

A FAIRLY wide variety of carbonaceous substances exist for use as "body" materials and for binders in the manufacture of industrial carbon products. There are several points to consider when making a choice of raw materials. Most factors have an economic bearing on the problem, and in this respect there have to be considered ease of availability; cost; quantity and quality required; and whether supplies are likely to be continuous or erratic. These economic problems are closely linked with the technical problems of producing a product from a mixture of substances under the best conditions, which have to be ascertained by experiment, coupled with experience, for any given combination of carbonaceous materials.

The raw materials used may be divided into three classes, according to the part they play in the process:

(1) "Body" materials, which are the carbonaceous particles making up the bulk of the product, include such carbons as: coals, cokes, natural graphites, charcoals, lampblack, and grog (rejected calcined or kilned carbon pieces, or crushed old electrode butts). Table I[1] gives the average analysis of such materials.

(2) "Binders," which serve to hold together the finely ground particles of the "body" materials, may be either liquid or solid substances, and include tars, oils, pitches, and both natural and synthetic resins. To some extent, molasses and sulphite lye find application in certain products. Table II[1] gives some physical properties of the more usual binders.

(3) Miscellaneous substances, which may be incorporated in the mixture to give certain specific physical or mechanical properties, include sawdust, used to induce porosity, and metal powders, for special bearing or brush applications. Some special mixtures will be considered in a later section.

TABLE I.—CHEMICAL ANALYSIS OF BODY MATERIALS

Material	Moisture %	Volatiles %	Fixed Carbon %	Ash %	Specific Gravity
Coal					
Anthracitic	2·4–14·0	1·5–8·5	65–85	6–18	1·5
Bituminous	1·8–19·0	6–40	49–79	2·8–19	1·3–1·4
Coke					
Beehive	0·5–1·5	0·3–3·0	80–95	4–20	1·9
By-product	0·7–3·0	0·6–3·3	79–92	7–16	1·7
Petroleum Coke	0·4–2·0	4·0–18·0	82–97	0·5–2	1·8
Retort and Gas Carbon	0·5–2·0	4·0–13·0	88–97	3–10	1·7–1·8
Pitch Coke	0·5–1·5	4·0–12·0	85–97	0·3–2·0	1·6–1·8
Natural Graphite	0·5–2·0	1·0–7·3	78–92	7·5–19·5	2–2·5
Wood Charcoal	1·0–10·0	1·0–10·0	84–97	1·0–4·0	1·3–1·9
Lampblack	0·6–3·0	3·0–7·0	90–96	0·6–10·0	1·7–1·8
Electrode Butts	0·2–2·0	0·0–0·2	85–94	6·0–14·0	1·9–2·2

TABLE II.—CHEMICAL ANALYSIS OF BINDERS

Material	Melting Point °C.	Free Carbon %	Coking Value %	Softening Temperature °C.
Coal Tar	Liquid	7–25	10–30	—
Gas-Retort Tar	Liquid	20–40	40–65	—
Coke-Oven Tar	Liquid	12–20	15–30	—
Pitch				
Soft	50–70	15–25	20–35	35–60
Medium	70–90	25–35	30–40	50–80
Hard	90–140	30–50	35–55	80–115

Body Materials

Coals and Cokes

Anthracite coal is widely used for this purpose, as it has the advantage of a high percentage of fixed-carbon coupled with a low content of volatile matter. Selected low-ash varieties may be used direct, but if the ash content exceeds about 2% some purification treatment is often advisable, such as leaching the ground anthracite in a hot caustic soda solution, followed by washing, as suggested by Escard[2]. This treatment reduces the ultimate ash content to about one fifth of its original value.

Bituminous coals have the disadvantage of containing a relatively low proportion of fixed carbon and a much higher percentage of volatile matter than anthracite. This necessitates calcination prior to use. However, the *metallurgical coke* manufactured from medium to strongly coking bituminous coals is commonly used as a raw material in the manufacture of hard carbon articles or carbon pastes, and of rammings such as are used for blast furnace refractories and for electrodes in some electro-thermal processes. Furthermore, both gas works and coke-oven plants provide a large proportion of the tars and tar oils which are used, either in their natural state as a binder, or as a raw material in the manufacture of lampblack and carbon black. The coking process also produces *gas retort carbon*, a deposit adhering to the walls of the carbonising chamber.

Petroleum coke, a residue from the distillation of mineral oils, is widely used in manufactured carbons. It is a hard, brittle, shiny, black substance and is very high in fixed carbon and low in ash. Unfortunately, the yield of this material only represents about 1% of the weight of the oil distilled. Sulphur may be an undesirable constituent of petroleum coke, depending upon the source from which the oil was obtained. Modern vacuum

Courtesy of The Morgan Crucible Co., Ltd.

Fig. 1.—A selection of Morganite carbon brushes for electrical machines.

distillation of oils prevents the formation of this deposit, and it is likely, therefore, that supplies of this material will slowly diminish. *Pitch coke* has similar qualities to petroleum coke and is produced by the destructive distillation of pitch derived from coal tar.

Graphites

Natural graphite occurs in several types varying in the texture, purity and physical characteristics which determine the use to which each may be applied. There are three recognised types of natural graphite: flake, crystalline and "amorphous." Despite the terminology, it is believed that all three are crystalline, the difference being in the size of the crystals, which is probably a result of the method and place of formation.

Flake graphite occurs as lustrous scales, frequently surrounded by gangue material. This makes purification difficult, but normal mineral dressing processes give a purified product containing at least 85% carbon (as graphite). The main deposits are in Madagascar and Ceylon and a very large proportion of this output is used for the manufacture of clay-graphite ("plumbago") crucibles and other refractory articles, and also for lubrication.

Crystalline or vein graphite occurs as wedge or rod-shaped pieces and chips, almost metallic in appearance, and usually found in vein deposits or pockets. The small surface area in relation to weight requires less bonding agent to "wet" the graphite particles. It is usually fairly pure in its natural state, and it may be further dressed to a high degree of purity. This material finds application in the refractory and crucible industries (often blended with the flake variety), and also in brush manufacture. Deposits are found mainly in Ceylon.

"Amorphous" graphite is found principally in Mexico and Korea. It appears dull and earthy but is really minutely crystalline. Although some of these graphites (Mexican) are high grade (86% carbon), most are inferior to the previous grades, and may be as low as 40% carbon. It is usually found associated with coal, shale and slate. Better grades are used for pencil, graphite grease and paste manufacture, whereas inferior grades are used for foundry facings and paint. Table III[1] gives the chemical analyses of some good specimens of natural graphite.

TABLE III.—CHEMICAL ANALYSES OF SOME NATURAL GRAPHITES

Locality	Ash %	Volatiles %	Fixed Carbon %	Specific Gravity
Ceylon	0·05	0·16	99·79	2·57
Mexico	2·15	1·19	96·66	2·17
Madagascar	1·76	0·82	97·42	—

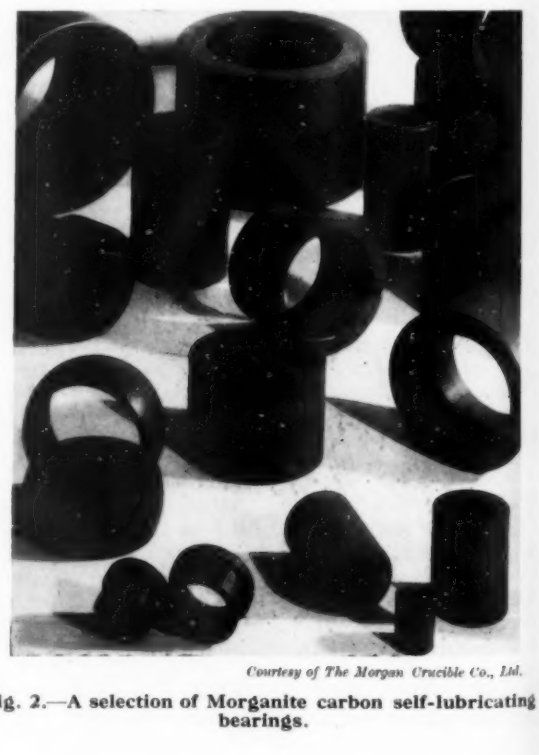
Charcoal

Wood charcoal is produced, either by burning wood excluded from air in covered heaps (called "meilers"), or by the more modern process of carbonising in closed iron retorts. The product, which retains the shape of the original wooden branches, is then crushed. This material is low in ash and high in fixed carbon, but it is comparatively costly and, therefore, is not widely used in the manufacture of carbon products.

A similar product from crude sugars (molasses) has limited application, but that from animal bones (bone-charcoal) is contaminated by phosphates, and, because of the purification necessary, it is not commonly used.

Carbon Blacks

Lampblack is a soft, flocculent carbon, whereas *carbon black* is comparatively hard. The latter is usually manufactured by burning natural gas (in the U.S.A.), or manufactured hydrocarbon gases, or even oils and tars, with a restricted air supply, using special burners of the batswing or fishtail variety. The flame is made to impinge on cool iron surfaces and the carbon product deposited thereon is scraped off continuously[3]. The average particle size as determined by the electron microscope[4] is stated to be 50–20 millimicrons, which places the material in the colloid category.



Courtesy of The Morgan Crucible Co., Ltd.

Fig. 2.—A selection of Morganite carbon self-lubricating bearings.

The purity is usually high, with fixed-carbon percentages ranging from 92 to 99, moisture 2–5%, ash 0·02–0·05% and volatiles 0·4–10%: the average specific gravity is 1·78. This material is only used to a small extent in manufactured carbon products for engineering purposes, but finds wide application as a reinforcing agent in the rubber industry (especially in tyres), where it may comprise up to 50% by weight of the product. The second greatest demand is for use in the production of printer's inks; other uses include the manufacture of paints, gramophone records, typewriter ribbons and carbon papers.

Lampblacks are manufactured in a similar manner to that employed for carbon black production, but only liquid or solid hydrocarbons are used as raw material, the most common being coal-tar oils, tar, mineral oils and resins. All are burnt with restricted air supply and the flames allowed to pass into a cool steel or brick chamber, when lampblack deposits itself upon the chamber walls. Modern furnaces are so designed that the lampblack-bearing gases have to pass over a number of baffles in flues, which help to deposit the carbon particles from the gas stream. This arrangement also ensures that each carbon particle has been heated to a sufficiently high temperature for any volatiles to be "cracked" or removed, thus giving a high grade product.

Such material has been shown by light and electron-microscope examinations to have a particle size in the range 100–400 millimicrons. Purity is quite high, with about 90–96% fixed carbon, up to 0·1% ash, 1–2% moisture and 2–10% volatiles. It is used for carbon muffle furnace insulation; in mixes used for carbon products; in the manufacture of hard metal carbides; and in the paint industry.

Acetylene black, made by thermal decomposition of acetylene at 800° C., gives an extremely pure product with more than 99% carbon; moisture, ash and volatiles totalling less than one per cent. X-ray studies[5] have shown this material to be partly graphitic and this is confirmed by the specific gravity value of over 2·0. It has higher liquid absorption powers than either carbon or lampblacks. Acetylene black is used in electrical brush manufacture and, in conjunction with pyrolusite, for making dry battery electrodes. A fairly recent application is its use (28%) in rubber mixtures to produce conductive rubber[6] for overcoming the effects of static electricity.

All the blacks discussed above have enormous surface areas, which require large amounts of binder for wetting sufficiently to enable the mixture to be moulded or extruded. If this were done and the fabricated article kilned, great shrinkage would occur, with inevitable cracking, so it is common practice to mill the calcined product and use this as the raw material for the final mixture.

Electrode Butts

Stub ends of electrodes arise mainly from aluminium extraction furnaces, since arc furnace electrodes are now usually threaded for joining a new section to the old. This material, which has already been kilned in manufacture and in service, is usually crushed, ground and used as "grog" (shrinkage controlling materials) in carbon mixtures used for electro-thermic carbons, smelting furnace linings, and, with petroleum coke additions, for electrolytic electrodes.

Courtesy of The Morgan Crucible Co., Ltd.

Fig. 3.—Morganite carbon gland rings for steam or water turbines.

Binding Materials

The usual binding materials are derived from the by-products of coal carbonisation, although special binders for certain applications are produced from other sources. In general, they are composed of elemental carbon and hydrocarbons in varying proportions. Since the volatile matter of a binder is driven off in kilning, the best binders from the standpoint of the finished article are those with the highest coking values, i.e., those which lose least during the kilning operation.

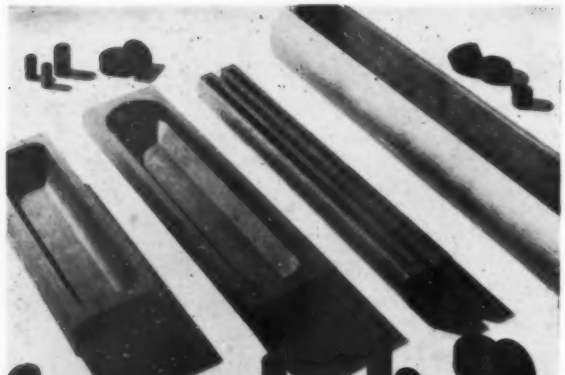
Coal Tars

Coal tars may be classified according to method of manufacture, e.g., gas-retort or coke-oven tar. They are black liquids of variable viscosity (depending on the type of tar) but usually quite viscous. The proportion of hydrocarbons is generally high (about 35%) and "free" carbon small (about 65%). The adverse proportion in favour of hydrocarbons is usually more marked in tars from by-product coke ovens ("free" carbon only about 20%) and this means that the tars from the latter source are more fluid than those from gas works.

As produced, these tars contain varying proportions of water, which must be removed before using as a binder, to prevent steam evolution in kilning. These dehydrated tars (containing about 0·5% moisture), in conjunction with pitch (to reduce porosity due to volatile loss), are widely used as binders for carbon mixes used for extruded electrodes, for carbon ramming, and for carbon brick and block manufacture by moulding. For high density carbon products, the high volatile content of tars is a distinct disadvantage.

Pitches

Pitches are residues from the vacuum distillation of coal tars for recovery of light and heavy oils. All are solids with melting points in the range 50–150° C. This property lends stiffness to a carbon mixture incorporating a proportion of pitch with the coal tar binder for extrusion. Many moulded products, and quite a few extrusions, use pitches exclusively as the binder. They are good binding materials, but the stiffness of the mixture necessitates high pressures for shaping, and the use of tars or oils in small proportions may be necessary to promote flow.



Courtesy of The Morgan Crucible Co., Ltd.

Fig. 4.—Morganite carbon tubes and boats for high temperature metallurgical applications.

METHODS OF MANUFACTURE

Preliminary Treatment

Before the actual shaping process, several preparatory processes are necessary to produce the homogenous mixture required to suit the forming operation, and to give the desired physical and mechanical properties to the finished product. These preparatory processes normally consist of some or all of the following (in chronological order): crushing, calcining, grinding, mixing or blending, and storing ready for use.

Crushing

Crushing is a necessary operation for anthractic or bituminous coals, for metallurgical and petroleum coke, and for electrode butts and kiln rejects. Jaw or roll crushers break down the materials to about 2 in. ring, prior to calcining if such an operation is necessary.

Courtesy of The Morgan Crucible Co., Ltd.

Fig. 5.—Morganite carbon piston rings as used in compressors demanding oil-free operation.

Calcination

Calcination removes volatile ingredients which would give a product of low density (high porosity) and high electrical resistance, the former characteristic usually being associated with low mechanical strength. The operation is usually carried out, in the U.S.A. and parts of Europe, using arc-resistance type furnaces with a bottom electrode, but in England and on the Continent, producer-gas-fired retorts, of the Woodall-Duckham and Glover-West types, or rotary calciners are more popular. Temperatures attained are about 1200° C. in the electric furnace and 800–1000° C. in the gas-fired furnaces. After cooling the "cokes" by controlled water sprays or inert gas chambers, the material is ready for grinding. The volatile content is now less than 0·5%.

Grinding

To obtain a high density and good mechanical properties in the finished product, proper grading of the carbon particles is necessary, on the assumption that the finer particles will fill the interstices between the larger ones, and thereby reduce the porosity. This grading may be done simultaneously with grinding, if the mill is so adjusted, and this is the more popular method, owing to its relative simplicity. An alternative method is to grind and screen the different carbon materials in the mixture to definite sizes, and then, later, blend them in the correct proportions by a further mixing process.

Ball and tube mills or gyratory grinders are widely used for the grinding process, and the type of plant is decided by the nature of the material to be ground.

The binders are prepared by grinding followed by melting, in the case of pitches, whereas tars merely require a small degree of heating to render them more fluid.

Mixing

The constituents in the mixture will depend on the required physical, mechanical, electrical and chemical properties of the finished material, and on the conditions of service. Thus, there are many brush mixes, but fewer compositions for electrodes, rods, tubes, and other extruded products. Moulded articles, again, have varying constitution depending on their application.

In general, the various proportions of solids (by weight) are fed simultaneously with the liquids (by volume) into the steam-heated mixers. The proportion of solids to binders is usually between 7:1 and 5:1. Heat is necessary to keep the mixture plastic. There are various types of mixers, some using rotating blades or paddles interlacing with similar ones on shafts rotating in opposite directions; others consisting of a horizontal drum with an axial shaft carrying inclined arms. The rotation of the shaft mixes the ingredients, and the slope of the arms carries the mixture forward to be discharged at the far end of the drum. An older type of mill, but one which is still used, is the Chilian or edge-runner mill, in which a large, rotating, shallow, heated, cast-iron pan drives by friction a pair of heavy rolls, mounted one on each end of a shaft carried at right angles to a vertical column situated in the centre of the pan. The mixture passes under the rolls by virtue of stationary deflecting plates in the bowl pushing it towards the path of the rollers. This method often combines grinding with mixing.

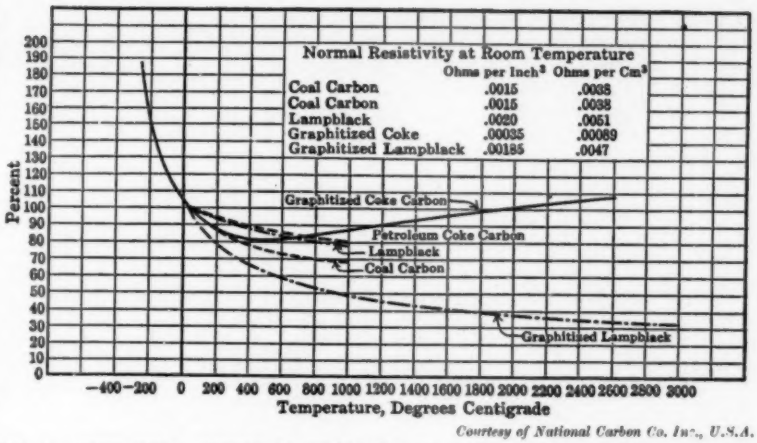
The ideal mix is one in which each carbonaceous particle has been coated with the *minimum* of binder, so that in the subsequent shaping process the pressure gives consolidation and cohesion.

Shaping

The warm mixture may now be given the shape of the finished article by one of three fabrication processes: (1) moulding or pressing, (2) extrusion, and (3) tamping.

Moulding

In this process, a calculated weight of mixture is fed into a steel mould and subjected to pressures of the order of 1–5 tons/sq. in. by means of a mechanical or hydraulic press.



Courtesy of National Carbon Co. Inc., U.S.A.

Fig. 6.—Percentage change in resistivity of carbon and graphite electrodes with variation in temperature.*

Extrusion

Extrusion produces the necessary shape by forcing a cylindrical slug of the warm mixture, contained in the steel cylinder of an extrusion press, through a steel die of the requisite shape, using a hydraulic-pressure-operated ram giving up to 2 tons/sq. in. Presses of 200–2,000 tons capacity are common.

Tamping

Tamping is the name given to the consolidation by hand ramming and pneumatic hammers of the mixture contained in a steel mould. The consolidation is usually done in stages, ramming a layer of 1–3 in. at a time.

In all cases, moulds or dies must be oversize to allow for the contraction which will occur on kilning. Moulding is said to give the highest density to the product, but the moulds can be very expensive if intricate shapes are pressed. The alternative is to press blocks and to machine the parts from these blocks. This is both difficult and costly with carbons, although it is frequently practised with electrographite.

Relative Merits

The extrusion process lends itself readily to the manufacture of rod, tubes, slabs and shaped sections, which, if required small, can easily be cut from the long lengths of the extruded material. Mechanical difficulty in handling long lengths of thin sections in the "green" condition must be considered.

With tamping, large blocks of irregular shape can be made with the collapsible moulds which are necessary for extracting such large masses from the moulds in the "green" state. By consolidating in layers, the packing density should be approximately uniform over the whole cross section. This would be difficult with the normal moulding technique, since very large pressures would be needed to consolidate to the centre, and this would require massive presses and moulds with corresponding expense.

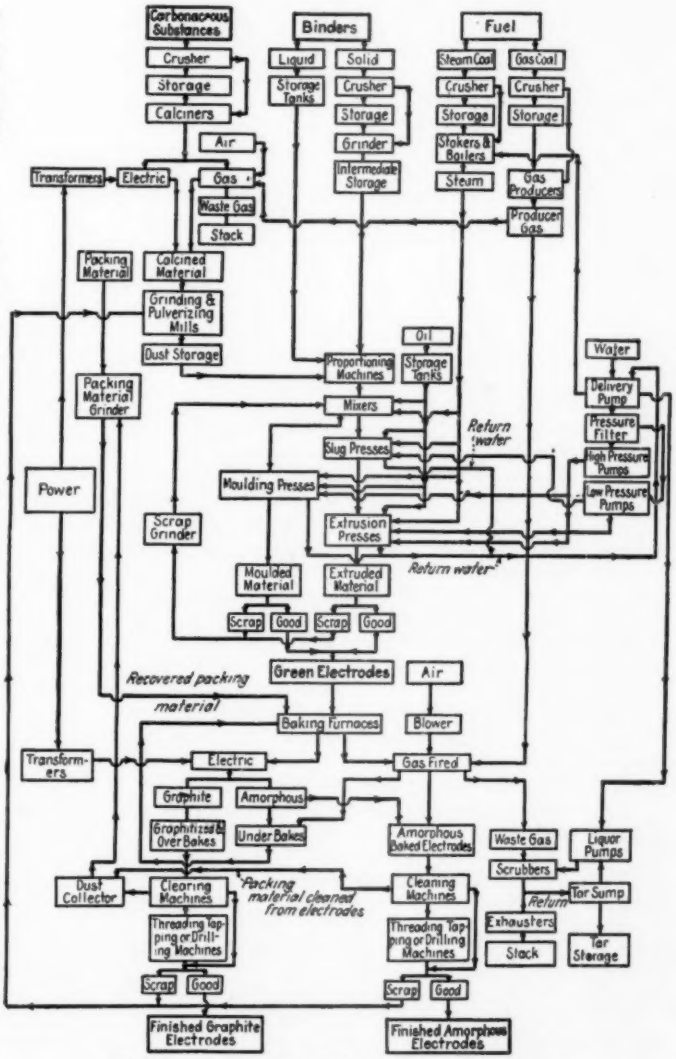


Fig. 7.—Flow sheet of electrode manufacture.

* Figs. 6 and 7 are reproduced from "Industrial Carbon" (Mantell), published by Van Nostrand in 1946.

Of the three processes, extrusion gives the biggest output and requires the least labour per ton of extruded product, provided the articles are required in large quantities of the same size and shape.

The shaped material, as it leaves the moulding press, extrusion machine, or tamping mould, is termed "green" carbon, and in this state it is quite fragile. The article may be carefully handled as soon as it has cooled, as the binder will then have stiffened, and in this state the pieces are sent for baking or kilning.

Kilning

The purpose of the kilning process is slowly to bring about distillation and "cracking" of the volatile constituents of the binder to form coke. As a result of this, each carbon particle of body material is firmly held together by a thin film of binder coke to give a strong dense product consisting normally of two phases.

The operation is carried out in an electric resistance furnace, which heats the charge by virtue of the resistance offered by the "green" carbon to the passage of the current through it, or in closed refractory brick muffle kilns, or pits, externally fired by producer gas or oil. One electrode-making company in the U.K. uses a tunnel kiln.

In all cases, the "green" carbons are protected from oxidation by a covering of crushed calcined coke or anthracite, or better still, petroleum coke of about 10 mesh. Large articles, such as furnace electrodes, blocks and slabs, may be kilned upright, but tubes and small diameter rod are supported vertically and fired in bundles. Small pieces receive their heat treatment packed in fireclay or graphite-clay vessels called "saggers," which simplifies unloading of the kiln when the baking is complete.

The kilning cycle will vary with the size and nature of the charge, but a typical example would be about 20–30 days for a 20–50 ton kiln. This would be made up as follows: 2–4 days loading; slowly heating to 1000–1300° C., in 7–12 days; soaking at temperature for ½–2 days; cooling almost to atmospheric temperature in 6–8 days; and unloading in 3–4 days.

The kilned articles, on removal from the furnace, require cleaning owing to the adhesion of the packing dust to the carbon surfaces. In this respect, it is imperative that this packing material shall be low in ash, or that the ash has a fusion temperature considerably higher than that used for kilning, otherwise it may form accretions on the product which will be difficult to remove.

Tumbling of circular pieces and brushing for flat articles are the usual cleaning processes. On inspection, any misshapen or cracked carbons are rejected, and are crushed for re-use as grog in subsequent mixtures.

With carbon electrodes, welding carbons, etc., electrical resistivity tests are carried out, and specimens not up to specification are rejected. It is found that the resistivity varies inversely as the elemental carbon content, directly as the percentage ash and volatile matter, and inversely as the density. Furthermore, the percentage change in resistivity of carbon (and graphite) electrodes is a function of temperature and of base materials. This is shown graphically in Fig. 6.

Owing to the very abrasive nature of most carbons, any machining, such as threading, drilling and tapping for electrode ends, or cutting and grinding to size, must be done with carbide or diamond tipped tools or abrasive wheels (mainly carborundum).

A typical flow sheet for the manufacture of carbon electrodes is shown in Fig. 7.

TYPES OF PRODUCT

The types of product made from industrial carbons are very numerous but the following examples will suffice to show the very wide field of application, both in the engineering industries and outside.

For the metallurgical industries, there are electrodes for arc and resistor furnaces; carbon paste for Soderberg electrode filling; welding electrodes; bricks and blocks for electric and blast-furnace linings, and carbon ramming for similar applications; iron runner brick shapes; ingot mould plugs and inserts; carbon furnace tubes; rods and boats for the hard metal carbide industries; foundry moulds; mould washes; cores; and riser rods.

In the chemical engineering field, there are pickling tank linings for steel sheet, strip and bar; paper pulp digestor linings; filter tiles and plates and aeration tubes (in very porous carbon grades), pipes and ducting; towers and tower packing rings for gas scrubbing; tubes as the earthed electrodes in electrostatic precipitation; and corrosion resistant pumps.

For electrical engineering there are lighting and dry battery carbons; brushes; carbon pile resistors; lift guides; trolley-bus inserts for current collecting; and telephonic and electronic applications.

Mechanical engineering applications include bearings; seals and piston rings; dash pots and plungers; and clutch thrust rings.

Miscellaneous products may be illustrated by glass moulds and forming tools, and bobbins and guides in the silk and nylon industries.

The necessary physical, chemical or mechanical properties of the various carbon products listed above will be discussed, with relation to their application or conditions of service, in a later article of this series.

REFERENCES

1 Mantell, "Industrial Carbon," 1946, Van Nostrand.
2 Escard, *General Electric Review*, New York, 1918, **21**.
3 Thorpe's Dictionary of Applied Chemistry, 1943, **2**, Longmans.
4 "The Particle Size and Shape of Carbon Blacks as revealed by the Electron Microscope," New York, Columbia Carbon Co., 1940, **2**.
5 Biscoe & Warren, *Jnl. App. Physics*, 1942, **13**, 364.
6 British Patent, 494, 058, 1937.

Symposium on Cathodic Protection

A SYMPOSIUM ON CATHODIC PROTECTION will be held at the Institution of Electrical Engineers, London, W.C.2, on Friday, November 13th, beginning at 9.45 a.m. and finishing at 5.30 p.m. Seven papers will be presented embodying experience gained in various parts of the world with the protection of ships, underground pipe, storage tanks and other structures used in contact with water or soil. Cathodic protection is a method which has been energetically developed during the last few years but has not hitherto had full public discussion in this country. The Society of Chemical Industry, Corrosion Group, in organising this Symposium is giving opportunity for such discussions.

MESSRS. WILLIAM JESSOP & SONS, LTD., and Messrs. J. J. Saville & Co., Ltd., have opened a new Area Office to direct selling activities in their Lancashire and Yorkshire territories. This is under the control of Mr. H. Carr and is located at York House, 12, York Street, Manchester, 2. Telephone: Manchester Central 9184.

Cement In Bulk To Site

Aluminium Alloy Pressurised Containers

ONE of the main features of a cement handling scheme developed by G. F. Shepherd & Son, Ltd., York, for use on the small contract, and which is claimed to make practical a potential saving of over 21s. per ton on all cement used over the first ton each week, is a cement tanker incorporating welded aluminium alloy containers. The system eliminates the need for cement bags and consequent bag disposal, labour on site unloading and on the mixer, waste in storage and handling, and saves money on site storage facilities. Furthermore, improved working conditions for the operative result from its use. The equipment consists of an advanced design of 30 m.p.h. 7-ton capacity cement tanker and a fully portable 10-ton capacity site silo complete with batch weight device.

The cement tanker, mounted on a 7-ton Bedford chassis and incorporating twin pressurised aluminium alloy cement containers designed for pneumatic delivery to silos on the site, is capable of elevating cement to heights in excess of 40 ft. if desired. No elevating equipment or source of power is called for on the site as the tanker carries its own engine-driven compressor.

The containers are stressed for a working pressure of 40 lb./sq. in. and have been tested and accepted by a leading insurance company for operation at this pressure. They are built up of panels of Noral M57S alloy which combines a high resistance to corrosion with good welding characteristics. Their spherical shape is not only the most efficient structurally, minimising weight, but also facilitates loading and discharge of the cement. A hinged manhole in the top enables the containers to be filled readily from overhead chutes and discharge is effected through a valve in the base designed for ease of operation at all times. The mountings of the containers constitute an important feature of the layout. They are constructed of Noral M57S alloy and have been successfully subjected to rigorous tests.

By the use of aluminium alloy and refinement of design, a striking reduction has been effected in the weight of the pressurised containers and ancillary equipment. Using the " Big " Bedford chassis, a payload of over 7 tons, which is within the maker's guarantee, has been achieved with an unladen weight of under 3 tons, thus qualifying for the 30 m.p.h. speed limit. The generous capacity of the pressurised containers permits the chassis manufacturer's maximum gross loadings to be used, and ensures full payload under working conditions. Under test these containers have actually received 8 tons 14 cwt. of loose cement, and under normal conditions one cement tanker can usually keep several silos supplied with cement on various sites in a given area. It is claimed that because the capacity of the containers permits the maximum gross loading to be carried under normal operating conditions, the cost of transporting and elevating on the site is no greater than that of the normal tipping lorry, equal utilisation being assumed.

Experience has shown that it is particularly important for the compressed air to be clean and free from oil : special attention has been paid to these points in the design of the compressor which is equipped with an air cleaner of generous proportions.

The London Aluminium Co. Ltd., of Witton, Birmingham, undertook the detailed design and construction of the equipment, in consultation with Northern Aluminium Co. Ltd.

Fielding Presses Arrive in Australia

A FIELDING 3,000-ton hydraulic forging press has been installed in the Australian Government's Forging Annexe at Granville, New South Wales, which is managed by the Australian Aluminium Co. Pty., Ltd. This press is of the four-column three-ram type, and is capable of operating at powers of 1,000, 2,000 and 3,000 tons. It is a downstroking press with top, bottom and moving tables of fabricated steel construction.

Power for its operation is provided by a Fielding air-hydraulic accumulator, fitted with electronic liquid level control system, and having a capacity of 220 gallons. Lubricated water is used as the pressure medium, and the working pressure is 4,500 lb./sq. in. Pumping equipment comprises two Fielding Type L.10 horizontal three-throw pumps which run at 150 r.p.m. giving a net output of 150 gal./min. at 4,500 lb./sq. in.

A further Fielding press which has now arrived in Australia is a 250-ton hydraulic single action blanking press built for Charles Hope, Ltd., of Brisbane. This press will be used for large metal stampings in the motor body building industry, and for general pressed-metal work carried out for customers all over Australia. Fielding and Platt are also building a 450-ton press for the same company.

The press which weighs 47 tons, is of the self-contained downstroking type, and is complete with hydraulic direct-pumping equipment. Oil is used as the pressure medium, and the total power on the main ram is 250 tons. The press comprises a main frame of heavy section unit welded fabrication, with a single differential-type ram, working in a forged steel cylinder and operating a large fabricated steel platen. Hydraulic die cushion cylinders are accommodated in the bed of the press. Power for operation is provided by a Fielding Type B.I. high-speed hydraulic pump, at a working pressure of 3,000 lb./sq. in., directly driven by a 40 h.p. electric motor.

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NEWS AND ANNOUNCEMENTS

The Platinum Metals Exhibition

THE INSTITUTION OF METALLURGISTS announce that H.R.H. The Duke of Edinburgh has graciously consented to open their Platinum Metals Exhibition at Grosvenor House on Monday, 19th October, 1953. The exhibition is being held to mark the Triple Jubilee of the British Scientist, William Hyde Wollaston's announcement of his discovery of the precious metal palladium. The exhibition, which will be open to the public from Thursday, 22nd October to Saturday, 24th October, will show the vital part played by the platinum metals in science and industry to-day.

Part-Time Technical Courses

THE Pure and Applied Chemistry syllabus of the Northampton Polytechnic, St. John Street, London, E.C.1, gives particulars of courses leading to the Associateship of the Royal Institute of Chemistry, and to the Licentiateship and Associateship of the Institution of Metallurgists. There are also organised courses on fuel technology, metal finishing and chemical engineering.

Besides the organised courses, there are two special lecture courses arranged for the Autumn Term. A series of 12 lectures on Refractories: Their Manufacture, Properties and Uses will be given by Mr. L. R. Barrett, on successive Tuesday evenings from September 29th to December 15th, the inclusive fee being £1 11s. 6d. The course is organised primarily to provide a detailed and up-to-date survey of refractories and the refractories industry for technologists engaged in the metallurgical fuels, carbonising, glass and chemical industries, but it is also suitable for students of metallurgy and other related branches of applied chemistry provided they possess the necessary fundamental knowledge of chemistry. The course is also suitable for those preparing for the examinations of the Institution of Metallurgists and of the Institute of Fuel.

The other special course consists of a series of eight lectures on Chemical and Metallurgical Thermodynamics, which will be delivered by Dr. O. Kubaschewski, on successive Wednesday evenings, commencing on September 30th. The fee for the course is again £1 11s. 6d. It is intended to discuss in this course the application of thermodynamics to practical problems of process metallurgy and other metallurgical topics. As the necessary thermodynamic equations will merely be given but not derived, it is desirable that students should have some knowledge of the fundamental concepts and methods of chemical thermodynamics. The significance of the thermodynamic functions (heat content, heat of formation, entropy, free energy) for the chemist will, however, be explained in detail and in a simple fashion. This will include partial molar thermodynamic quantities, i.e., the thermodynamic properties of solutions. The various thermochemical methods (calorimetric, electrochemical, equilibrium pressures) will be described to some extent, and particular attention will be paid to the estimation of unknown thermochemical values. Finally, some practical problems will be selected and discussed, such as the deoxidation of steel, production of rare metals, and determination of phase boundaries from thermochemical data.

Non-Ferrous Metals Industry in India

INDIA'S non-ferrous metal industry is still in its infancy, although the country has considerable non-ferrous mineral wealth. With the object of focusing attention on the present state of the industry and of discussing ways and means of stimulating its growth to meet present and future requirements, it has been decided to hold a symposium on " Non-Ferrous Metal Industry in India " in January, 1954, under the auspices of the National Metallurgical Laboratory.

The subjects to be considered include : (1) non-ferrous mineral wealth of India ; (2) beneficiation, extraction and refining of non-ferrous metals ; (3) applications of thermodynamic principles to the extraction and refining of non-ferrous metals ; (4) melting and foundry techniques for non-ferrous metals and alloys (including refractories used) ; (5) thermal treatment and fabrication techniques for non-ferrous metals and alloys ; (6) application of powder metallurgy techniques to non-ferrous metals and alloys ; (7) protective coatings for non-ferrous metals and alloys, such as cladding, plating, electrolytic and hot dip coatings, etc. ; (8) present status and scope of future expansion of the non-ferrous metal industry in India in relation to the Government of India's Five Year Plan ; (9) economics of the Indian non-ferrous metal industry—utilisation of by-products and reclamation of wastes ; (10) researches into the development of modern non-ferrous alloys.

Those wishing to present papers should forward an advance copy to Dr. B. R. Nijhawan, Deputy Director, National Metallurgical Laboratory, Jamshedpur 7, India, before November 15th, 1953, so that the final programme, abstracts of papers, etc., may be drawn up and circulated.

Hardness Testing Conference

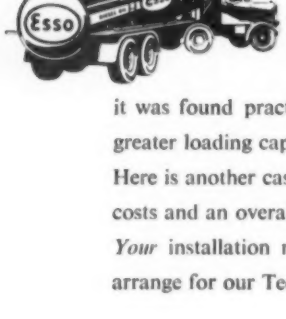
THE next special conference of the Sheet and Strip Metal Users' Technical Association will be held in the City Hall, Sheffield, October 14th–16th, and will be devoted to consideration of the numerous aspects of hardness testing of particular interest to the sheet and strip metal user. One particularly interesting and important part of the conference will be the exhibition of hardness testing machines and equipment which will be staged by the manufacturers throughout the period of the conference. These exhibits will be of considerable technical interest and members and others attending the conference or otherwise in Sheffield at that time will be very welcome to visit the exhibition and discuss the merits of the different machines with the exhibitors.

Coke Oven Plant Contract

THE National Coal Board announce that they have placed an order with The Woodall-Duckham Construction Co., Ltd., London, for an extension to the coking plant at their Monkton Coke Works, Hebburn-on-Tyne. The new plant will more than double the output of the existing plant, and will comprise a new battery of 33 W-D Koppers Combination Circulation Gas Gun Coke Ovens with a daily throughput of about 700 tons of coal, new ovens coal bunker, new coal handling plant serving both the new and the existing ovens coal

THEY CHANGED TO FUEL OIL

OUTPUT GREATLY INCREASED



By converting from solid fuel to fuel oil for firing his beehive kilns, a well-known manufacturer of glazed ceramics has found that the improved combustion and greater control obtained from oil firing has enabled him to reduce the firing period from 84 to 62 hours. In addition it was found practicable to remove part of the bag wall from each kiln, thus obtaining greater loading capacity for each firing.

Here is another case where conversion to Esso Fuel Oil has resulted in a reduction of labour costs and an overall increase in output.

Your installation may be particularly suited for conversion to fuel oil firing. May we arrange for our Technical Representative to call and discuss the matter with you.

It pays to say ESSO FUEL OILS

ESSO PETROLEUM COMPANY, LIMITED, 36 QUEEN ANNE'S GATE, LONDON, S.W.1

bunkers, extensions to the coal blending bunkers, new coke handling and screening plants for both the new battery and the existing battery, extensions and replacements to the by-product recovery plant, gas dilution and additional gas boosting equipment, a completely new liquor flushing system, a crude benzol plant, and new water cooling and circulating systems.

Corrosion Course for Engineers

A SERIES of 11 lectures which, although primarily intended as a short course in corrosion for chemical, mechanical and civil engineers, should be of value to others who are interested in the subject, has been arranged by the Department of Metallurgy at Battersea Polytechnic. The lectures, by specialists in each field, will be given at 7 p.m. on successive Thursday evenings from October 1st to December 10th, and the inclusive fee for the series is 25s. The aspects to be considered include electrochemical principles of corrosion; choice of metals for particular forms of service; protection by metal coatings; corrosion inhibitors; cathodic protection; protection by paints; and temporary protectives, packing and storage. Further particulars can be obtained from the Secretary (Corrosion Course), Battersea Polytechnic, London, S.W.11.

Refresher Courses for Works and Plant Engineers

THAT the comprehensive refresher courses for works and plant engineers arranged by the Education Committee of Incorporated Plant Engineers are now an established and markedly successful feature of industrial education is shown by the record number of enrolments wherever they are held. Commencing in 1949 at Bristol University where there were 233 enrolments, every subsequent course has commanded progressively greater support. Thus in 1950 at Nottingham University there were 312, in 1951 at Birmingham 373, whilst at Liverpool University and at Glasgow last year the enrolments for the course reached the remarkable figures of 392 and 405 respectively.

The Education Committee announces that for the coming winter session it has arranged a comprehensive Refresher Course comprising 20 weekly lectures to be held at Leeds University on Thursday evenings, commencing on October 15th. The course is designed to encourage the most effective use of existing knowledge and to promote the application of up-to-date techniques in works engineering practice over a wide field. It covers an extensive range of subjects of everyday importance to works and plant engineers, treated by specialists drawn from industry, and particular regard has been paid to the requirements of the area. The fee for the course is three guineas and copies of the syllabus and full particulars may be obtained from the Secretary to the Refresher Course, The Department of Engineering The University, Leeds, 2. (Tel.: Leeds 31751, Ext. 232).

O.E.E.C. Suspends Molybdenum Restrictions

RESTRICTIONS on the use of molybdenum in case-hardening and constructional steels in Member countries of the Organisation for European Economic Co-operation have been suspended by a decision of the Council of the Organisation. These restrictions were imposed in May, 1952, as a result of shortages of molybdenum and nickel on world markets. The new decision does not apply to nickel, for the present improvement in the supply situation is not sufficient to justify the abolition of the restrictions in force. The Council has instructed the Iron and Steel Committee to follow closely the supply position for molybdenum, and to make appropriate proposals for the final repeal of restrictions or for their reimposition, should the supply position make it necessary.

Personal News

RT. HON. THE LORD RIVERDALE, G.B.E., has resigned as Chairman and Director of High Speed Steel Alloys Ltd., Widnes, owing to indisposition, a decision which the Board of the Company received with the very greatest regret. Lord Riverdale has been Chairman of the Company since its formation in 1914, having been a prime mover in its creation when it was necessary to ensure a supply of tungsten to this country and terminate dependence on Continental supplies. The Board have elected MR. LEWIS CHAPMAN as Chairman in succession to Lord Riverdale.

MR. J. SAVAGE has been appointed Head of B.I.S.R.A.'s Physics Department with effect from October 1st, 1953. As Head of the General Physics Section of the Physics Department since 1947, Mr. Savage has been closely associated with the Association's work on continuous casting. He has been Deputy Head of the Department since 1948.

MR. H. DREW, Chief Engineer of Vauxhall Motors, Ltd., has been appointed Assistant Chief Engineer of General Motors Overseas Operations, with headquarters in Detroit. MR. M. PLATT, formerly Vauxhall's Executive Engineer, succeeds Mr. Drew as Chief Engineer.

MR. H. N. G. ALLEN has been re-elected Chairman of Council of the British Internal Combustion Engine Research Association for the current year.

MR. J. C. K. SHIPP has recently joined The English Electric Co., Ltd., to become the Group's Aviation Representative in the United States. Mr. Shipp worked previously at the Royal Aircraft Establishment and the Ministry of Aircraft Production. For a time he was head of the Civil Aircraft Flight Testing Department at the Aeroplane and Armament Experimental Establishment, Boscombe Down, Wilts. In 1950 he was appointed West Coast Representative of the British Joint Services Mission in America, and in 1952 became Assistant Director of Technical Development (Planning) in the Ministry of Supply.

MR. C. R. PIPE has been appointed Chief Metallurgist at the R.T.S.C. Laboratories, near Aylesbury, the joint research organisation of Richard Thomas & Baldwins and the Steel Company of Wales.

SIR JOHN DUNCANSON, who was Controller of Iron and Steel from 1942 to 1945 and Commercial and Technical Director of the British Iron and Steel Federation from 1945–1948, has been appointed a Director of Fescol, Ltd.

DR. B. R. NIJHAWAN has been appointed Deputy Director of the National Metallurgical Laboratory, Council of Scientific and Industrial Research, Jamshedpur (India). Dr. Nijhawan attended the Fifth Empire Mining and Metallurgical Congress in Australia last April as a delegate of the Government of India.

PARTICULARLY GOOD INSTRUMENTS FOR THE PARTICULAR

The other day we visited the metallurgical laboratory of one of the biggest motorcar manufacturers in the country where we discovered a large REICHERT metallurgical camera microscope which had been in daily use for near enough 20 years. Frankly, we were amazed (although we know RIECHERT workmanship) and especially so when we were told that this old veteran was still producing excellent work.

We have now added to our range of Reichert instruments a number of other outstanding products in the field of metallurgical instrumentation and shall be glad to forward full particulars on request. Incidentally, we shall be exhibiting some of our instruments on October 14th–16th on the occasion of the Hardness Testing Conference at the City Hall, Sheffield, and hope to have the pleasure of welcoming you at our stand.

Buehler

Specialised Equipment for the preparation of metallurgical specimens. Hydraulic Embedding Presses. Grinding and Polishing Machines. Diamet-Hyprez Polishing Compounds.

REICHERT WIEN

Large Research Metallograph Type 'Me A'. Universal Camera Microscope 'Me F' (shown above). Micro Hardness Tester of most advanced design. New incident light phase contrast equipment employing standard coated objectives.

ZEISS WINKEL

New Inverted Metallurgical Bench Microscope available with monocular or binocular body and photographic attachment.

SHANDON

SHANDON SCIENTIFIC COMPANY

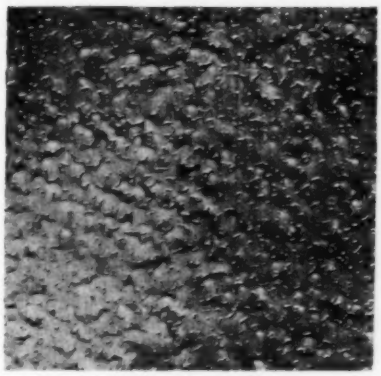
6. CROMWELL PLACE LONDON S.W.7. *Tel: Knightsbridge* 1131

RECENT DEVELOPMENTS
MATERIALS : PROCESSES : EQUIPMENT

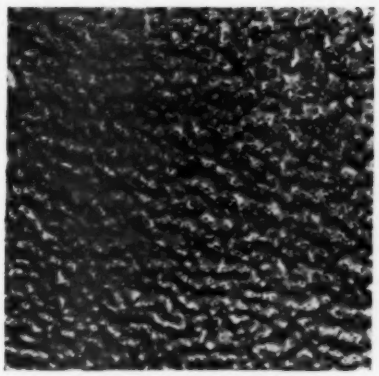
Embossed Aluminium Sheet

The embossing of aluminium sheet has practical advantages over the normal bright rolled finishes for many industrial and domestic applications.

Apart from its inherent attractive appearance, the embossed finish is less apt to show scratches, dents or other marks arising from rough usage and is, therefore, admirably suited for uses such as kick plates, skirtings and surrounds. The embossing operation itself work hardens the metal, and by increasing the overall thickness of the sheet has a considerable stiffening effect, so that embossed sheets are of particular advantage for flat panels such as wall coverings or the sides of containers.



Light stucco finish



Heavy stucco finish

A feature of the embossed surface is that it breaks up light reflections and greatly improves the appearance of panel work on unpainted fabricated structures. The least inequality on such surfaces, for example along the line of riveted joints, tends to show up undesirably with bright metal surfaces. Painting of aluminium is frequently specified, more to mask such defects than to give greater durability, but embossed aluminium can render this expense unnecessary for many applications. For corrugated and other roofing sheet, the embossed finish diffuses reflected light while retaining the full reflectivity and hence the heat insulating properties of aluminium.

Aluminium sheet with an embossed finish is now being produced by The British Aluminium Co. Ltd., two patterns being available for flat sheet and one for Rigidal corrugated sheet. The distinction between the two patterns—light stucco and heavy stucco—is in the depth of the impression, and both are available in commerical purity (99%) aluminium and in B.A. 60 alloy, in soft and half hard tempers, and in gauges from 24 s.w.g. to 18 or 16 s.w.g. These tempers are those of the sheet before embossing, the finished sheets being somewhat harder due to the work hardening effect of the embossing operation. The maximum sizes of sheet available are 8 ft. × 4 ft. and 8 ft. × 3 ft., depending on alloy, gauge and temper. Embossed Rigidal sheet is available in all three standard Rigidal profiles; 3 in. pitch, Mansard pattern, and trough section.

*The British Aluminium Co., Ltd., Norfolk House, St. James's Square, London, S.W.*1.

Electronik Molten Metal Temperature Recorder

Honeywell-Brown announce that a molten metal temperature recorder has been added to their standard range of industrial instruments. Initially developed to meet the needs of the steel industry it is in circular chart form and is ideally suited for making rapid temperature checks, by immersion thermocouples, for any molten metal.

All ranges, according to application, are available, and the rapid speed of response of 5½ seconds for the full 28⅝ in. of circular scale permits the temperature to be measured and recorded very rapidly. To enable temperature changes to be accurately analysed, a chart speed of one revolution in four minutes is employed and, to avoid chart wastage during off-measurement periods, the chart drive is switched off when the instrument records below a pre-set temperature.

Other features include push button standardisation with a device for driving the pen to mid-scale immediately prior to this operation, for thermocouple circuit proving, and a thermocouple " burn out " safety feature giving a down scale " pen drive " when this fault occurs. A similar instrument is also available in strip chart form.

Honeywell-Brown Ltd., 1, Wadsworth Road, Perivale, Greenford, Middlesex.

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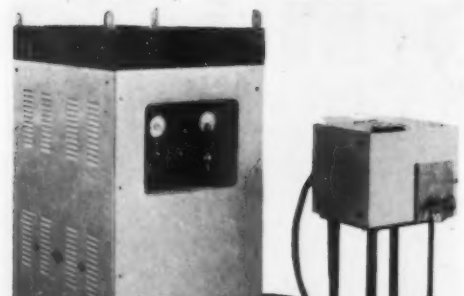
5 Kw Induction Heater

The new Airmec 5 kW. induction heat generator, Type 850, is suitable for use in soldering and brazing, hardening, annealing and melting. An indication of its capacity in melting is given by the fact that 1 lb. of nickel pellets (M.P. 1452° C.) can be melted in a plumbago crucible in 8 minutes. Both manual power control and facilities for automatic power control have been incorporated, thus enabling a high standard of heating precision to be obtained, particularly in repetitive operations. The output power may be made independent of supply voltage charges, or may be made to vary as a function of any desired quantity such as temperature.

A remote work unit is provided which may be operated fixed to the side of the generator unit, or up to 12 ft. away in any convenient position. This arrangement enables articles to be heated at a distance from the generator without loss of power. When necessary, a third small unit, a capacitor unit, may be added which makes possible applications which could not otherwise be carried out with a generator of this rating.



The difficulty of a fixed output impedance limiting the number of applications in which the optimum power can be generated to a very few, is overcome by arranging that the whole low impedance secondary coil can be replaced in two or three minutes by a medium or high impedance coil. In difficult applications an increase in up to double the power can be obtained by tuning the work coil by means of the capacitor unit. When a very high impedance is required, the secondary coil is removed completely and replaced by a heat insulating cylinder: the tank coil is then employed as an induction oven. This arrangement is particularly suitable for heating metals in a vacuum as, although coupling is rendered difficult by the large distance between the metal and the actual coil, the full 5 kW can still be generated in the work.

Airmec, Ltd., High Wycombe, Bucks.

Surfacing by Unionmelt

An entirely new range of Fusarc Continuous Electrodes, known as the Fusemelt series, has been announced by Fusarc, Ltd. They are specially designed for the deposition of wear-resisting and hard-surfacing alloy weld metals by the submerged arc Unionmelt process. Continuous Electrode—embodying the well-known spiral-wound patented construction—is used with Unionmelt powder of appropriate grades. The process enables a wide range of electrodes to be easily and economically produced to customer's requirements for particular hard surfacing applications, covering a hardness range from 250 to 700 D.P.N. Unionmelt welding is particularly suitable for surfacing applications because of the smooth finish of the deposit, and Fusemelt electrodes have the advantage of reducing penetration into the parent metal. For many applications, little or no shaping of the deposit is required after welding.

Fusarc, Ltd., Team Valley, Gateshead.

Raskin Presses

GEORGE COHEN SONS & CO. LTD. announce an interesting development in the range of power presses manufactured by Hubert Raskin, for whom they have acted as sole distributors in Great Britain for nearly twenty years. Raskin rigid open-fronted presses can now be supplied with a special device to enable folding and multiple punching operations to be carried out on sheets up to

8 ft. long. The top half of the folding tool slides on the external surface of the guides, which latter are machined parallel to the prismatic guides of the ram. As shown in the illustration, special outrigger jacks are employed to support the lower half of the tool. The whole mechanism may be removed from the press in a matter of minutes, after which the machine may be used as a standard press.

The presses are fitted with 4-speed motors and, as the number of strokes per minute may be varied by push-button controls from sixty down to fifteen, shallow drawing operations as well as stamping, multiple punching, and folding can be performed.

It is not claimed that a Raskin Press fitted with the new attachment will perform *all* duties of a press brake or a multiple punch (in addition, of course, to those of a standard press) but it will do many of them.

George Cohen, Sons and Co. Ltd., Sunbeam Road, London, N.W.10.

CURRENT LITERATURE

Book Notices

STATISTICAL YEAR BOOK FOR 1952. PART I—UNITED KINGDOM STATISTICS

Published by the British Iron and Steel Federation, Steel House, Tothill Street, London, S.W.1. 7s. 6d.

THIS volume gives information concerning the U.K. iron and steel industry in all its aspects. Besides iron and steel production, finished steel deliveries and the use of raw materials, the tables give details regarding imports and exports, prices, stocks and employment in the industry. They are grouped according to subject, beginning with iron ore and working through the various sections of the industry to the overseas trade statistics. For the convenience of the general reader, two summary tables at the beginning give information for a long run of years. The first brings together the main statistical series relating to iron ore, coke, pig iron, scrap and steel. The second sums up the information regarding the supply and disposal of steel; and shows, for example, that the supply of steel available for consumption in the United Kingdom (excluding exports) rose from an annual average of 5,050,000 ingot tons in 1921–25 to 9,240,000 tons in 1938 and to 15,900,000 tons last year.

An attempt has been made, with the production of each succeeding *Year Book*, to improve and extend the services offered. This year, for instance, in the finished steel section, in each of the main product groups, figures are given for gross deliveries, deliveries of conversion material, exports and, finally net home deliveries in 1951 and 1952. These figures have not previously been given in this form. Again a new analysis is given of U.K. exports by values tracing the growing contribution made by the steel producing and consuming industries to the export drive. Additional information is available regarding consumption of imported ore, and a complete picture is presented of the industry's coal consumption. In a different sphere, the detailed analysis of steel furnaces in existence for the first time sub-divides electric furnaces into the two categories of arc and high frequency.

As against these additions, statistics on the distribution of finished steel by industry had to be abandoned when the Government re-introduced the steel distribution scheme in February, 1952. Since the relaxation of control in May of this year, preparations have been made for statistics to be collected again on this basis, and it is hoped to include an analysis for at least part of 1953 in the 1953 *Year Book*.

ALUMINIUM AND ITS ALLOYS IN BUILDING

76 pp., numerous illustrations, paper covers. The Aluminium Development Association, London, 1953. 3s. 6d.

IN this publication examples are shown of the uses of aluminium in specific types of building, e.g. industrial buildings, universities and schools, dwelling houses, shop and store fitting, farm and horticultural buildings, street furniture and churches. Many of these examples also form case histories and provide interesting stories of the long life of aluminium in varying circumstances. Durability is, of course, one of the factors emphasised in the subsequent section of the book on "The Case for Aluminium" where the advantages of high strength/weight ratio and of a range of extruded sections (giving increased scope to the designer) are among the points considered. There follows a brief description of the characteristics of aluminium in relation to building usage, and cross references are made to the series of A.D.A. Information Bulletins covering special subjects such as surface finishes, extruded sections and aluminium castings. The concluding section of the book is a series of notes on erection, installation and maintenance and here again readers particularly interested are referred to other A.D.A. publications for fuller details.

INDEX TO THESES ACCEPTED FOR HIGHER DEGREES IN THE UNIVERSITIES OF GREAT BRITAIN AND IRELAND. VOL. I: 1950–51

Published by the Association of Special Libraries and Information Bureaux 4, Palace Gate, London, W.8. 25s. (by post 25s. 6d.).

WHILE hundreds of new books and journals dealing with British research appear in our libraries daily, it is something of a paradox that much of our most scholarly writing is never published. In this country the university thesis exists in typescript only, and, once accepted, often becomes just an unrecorded archive. The thesis, prepared for a higher degree, is written by someone who has graduated in a field of learning and has subsequently carried out research with the finest facilities and under the direction of experienced scholars. It comprises approved results of undoubted importance which ought to be known.

There is no doubt about the demand for this knowledge, and in many countries publication is the rule. At the present time, however, there is no likelihood of a change of practice in the British Isles. The public may consult the typescript, and may sometimes borrow it or obtain photocopies, but when only about half our universities publish lists of the theses in their keeping, it is difficult for the research worker to become familiar with what has been written.

The need for a comprehensive list has been recognised for many years and now, with the publication by Aslib of this volume, there exists the first part of what is to be an annual national bibliography. Volume I covers the period 1950–51, and the editor, Mr. P. D. Record, M.A., F.L.A., has listed some 2,200 theses. All subjects have been covered and each entry contains the title of the thesis, the author's name and university, and a note indicating availability to the public.

Trade Publications

WE have received from R. & J. Beck, Ltd., a copy of the new edition of their general catalogue of microscopes and accessories. A number of microscopes of metallurgical interest are described including the No. 50 Universal Microscope, which is fitted with binocular and monocular vision, and on which examination can be made by light and dark field illumination. This is made in

three forms, one for transparent objects, one for opaque objects, and one for both transparent and opaque work. Copies may be obtained from 69, Mortimer Street, London, W.1.

MAGNUMINIUM TECHNICAL DATA, has recently been issued by High Duty Alloys, Ltd., Slough, with the object of assisting designers to select the most suitable Magnuminium alloys for particular requirements. To this end, the physical and specified mechanical properties of the magnesium alloys—both wrought and cast—manufactured by the company are listed. In addition, details are given of related proprietary alloys.

A REVIEW of recent technical developments in the production, properties and applications of copper and its alloys, with a comprehensive bibliography, is published twice a year, in January and July, by the Copper Development Association, under the title *Technical Survey*. The second of these is now available, and a copy will be sent free of charge upon request to anyone who is interested, and those who wish to take advantage of this valuable service should write to the Association at Kendals Hall, Radlett, Herts., asking for their names to be placed on the mailing list.

FOUNDRY SERVICES, LTD., announce the first issue of their new publication called *Foseco Foundry Developments*. In it is given news of various development projects on which the company is working, as well as useful facts and figures accumulated during such research. It is hoped that this will prove of help to the foundryman and metallurgist in their efforts to improve melting and casting processes and reduce production costs. *Foseco Foundry Developments* will be published as the need arises and is available free of charge to anyone interested by writing to Foundry Services Ltd., at Long Acre, Nechells, Birmingham, 7.

THE products of the Charles Davidson Branch are dealt with in two new publications issued by General Refractories, Ltd., Genefax House, Sheffield, 10. A twelve page booklet deals with heat and acid resisting materials of the Obsidianite and Losol grades. The former are basically aluminium silicate fired to an extremely dense texture and containing the correct proportion of chemically inert vitreous bonds: the chemical characteristics of Losol are similar, but the constituents are of exceptional purity. These materials are used in the lining of pickling tanks, acid concentrators and other chemical plant and for acid-proof flooring. Details are given of the sizes of the available bricks and special shapes. High alumina and fireclay refractories are featured in the second leaflet and technical details are given of the Alumantine range which are designed for use at high temperature under conditions of chemical attack and abrasion in the cement, lime, chemical and metallurgical industries. The four grades available range from 40% to 73% alumina. For less severe conditions, Hysilyn or Adamantine fireclay refractories may be used, the former up to 1,300° C. and the latter up to 1,100° C. Reference is also made to Alumantine and Hysilyn plastic fire cements for jointing and patching.

A COMPREHENSIVE source of reference on Ferroxcube magnetic ferrites has recently been issued by the Components Division of Mullard Ltd., Century House, Shaftesbury Avenue, London, W.C.2. This 46-page publication should prove of considerable value to the equipment designer. It comprises five chapters: the first gives an historical survey of magnetic ferrites followed by details of their physical structure, whilst the second deals with the electrical and magnetic properties of Ferroxcube. Subsequent chapters are devoted to the mechanical properties of the material, application data and standard core shapes and dimensions.

W. EDWARDS & Co. (London), Ltd., Worsley Bridge Road, Lower Sydenham, London, S.E.26, have published several new brochures dealing with sections of their range of high vacuum equipment. In one of these the complete range of Speedivac rotary pumps is illustrated and described, including the latest additions to the range, the two stage 2S150 and the single stage 1S450, displacing 5 and 15 cubic feet per minute, respectively. Performance curves and figures are shown for each pump together with useful notes concerning non-return valves and moisture traps. The important aspect of trapping contaminating vapours which prove harmful to the rotary pump interior, is dealt with in a six page leaflet. Three models are shown which can be fitted to the Speedivac pumps whilst others are suitable for placing in the vacuum line. The latter half of the list describes and illustrates the mercury vapour traps which are available for the Speedivac mercury diffusion pumps. The technique of vacuum coating, notes on some of its present day uses and the complete range of plant manufactured for both evaporation and sputtering, are described in an eight page brochure. Each plant is illustrated separately, with the various jig arrangements, and a specification table shows their technical characteristics and pumping down times. The series of "Vacuum Notes" advertisements has been reprinted and bound in booklet form, making an extremely useful addition to the data kept by all laboratory workers and production engineers concerned with high vacuum equipment. The most common problems encountered in the use of vacuum are described with the aid of diagrams.

A NEW edition of "Notes on Machining the Nimonic Series of Alloys" has just been issued, containing additional information on drilling and extended to cover the newer alloys, Nimonic 90 and 95. This publication provides general guidance based on practical experience and makes reference to various tools and cutting oils which have been proved successful. Suggested speeds and feeds are given for each operation, together with diagrams of profiles and tool forms taken from actual machining operations. In general, essential requirements for successful machining are (*a*) the use of tools which are sharp and will resist abrasion, and (*b*) slow speeds and a smooth drive with ample power to prevent stalling. Copies of this useful handbook are available from the Publications Department, Henry Wiggin & Co., Ltd., Thames House, Millbank, London, S.W.1.

THE 1953 Aluminium Development Association Directory of Members gives the names of the Members of the Council, a brief statement of the constitution and objects of the Association and the names, addresses and other particulars of its member companies including, where applicable, associate or subsidiary companies. In each case a short description is given of the activities and products of the company. By means of an index of products classified under aluminium and aluminium alloys readers are referred to all member companies producing any particular product.

CAMBRIDGE TEMPERATURE CONTROLLERS

ELECTRICALLY OPERATED

INDICATING CONTROLLERS
INDICATING ZONE CONTROLLERS
INDICATING ALARMS
RECORDING CONTROLLERS
POTENTIOMETER CONTROLLERS
POTENTIOMETER ZONE CONTROLLERS
TIME-TEMPERATURE CONTROLLERS
HEAT SENSITIVE ELEMENTS
AUTOMATIC VALVE GEAR, etc.

MECHANICALLY OPERATED

DIAL OPERATED
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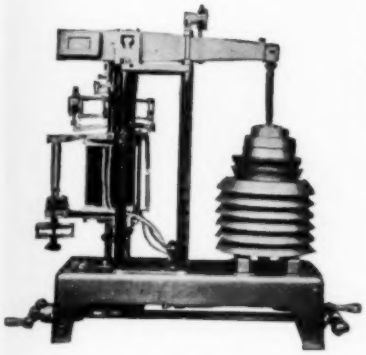

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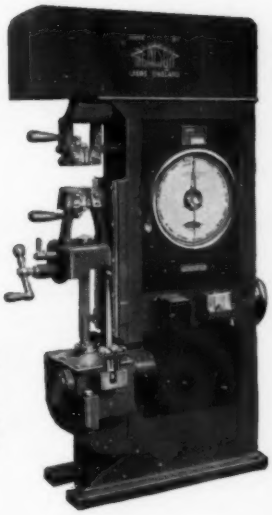

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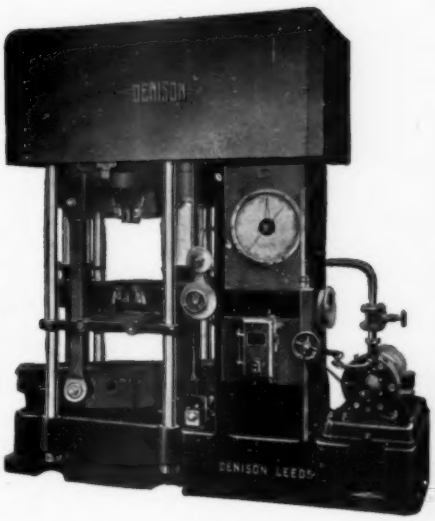

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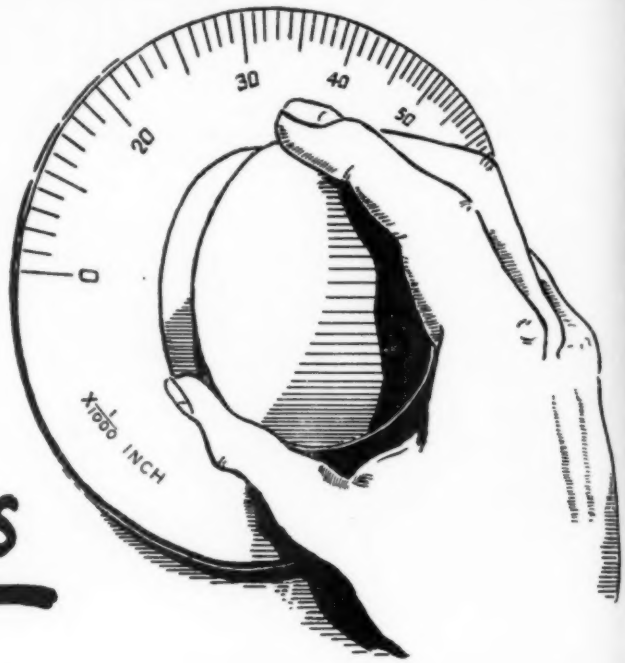

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SEPTEMBER, 1953 Vol. XLVIII, No. 287

The Photometric Determination of Impurities in Tin

By W. C. Coppins, M.Sc., A.R.I.C., and J. W. Price, Ph.D., F.R.I.C.

Tin Research Institute, Greenford, Middlesex

Following on a previous paper, describing the photometric determination of arsenic and antimony in tin, the authors detail methods for the photometric determination of ten further elements which may be present as impurities in commercial tin. They are: lead, copper, bismuth, iron, nickel, cobalt, aluminium, zinc, cadmium and sulphur.

METHODS for the photometric determination of arsenic and antimony in tin have recently been described by the present authors.[1] The photometric determination of ten further elements that may be present in small amounts in commercial tin has now been investigated, and the procedures that have been found most suitable are described below.

A spectrophotometer was used for measurement of the colours, but a filter photometer is equally suitable in most cases, and the appropriate filters are mentioned under the individual methods. Where possible, the methods have been checked against standard samples. In this connection, the spectrographic analysis samples available from the National Bureau of Standards have been particularly useful.

As most of the methods require the preliminary removal of the tin by volatilisation of the bromide, it is often possible to determine a number of impurities in a single sample, by taking suitable aliquots of the solution of the residue after removal of the tin. For example, a sample of 5 g. may be treated with hydrobromic acid and bromine to remove the tin, and the residue dissolved in nitric acid and diluted to 50 ml. Then 10 ml. aliquots may be used for the determination of iron, nickel and cobalt, 5 ml. aliquots for copper and cadmium, a further 5 ml. diluted to 50 ml. and of this diluted solution 5 ml. taken for lead and 25 ml. for zinc. A separate sample is necessary for the determination of bismuth, as removal of the tin must be accomplished in the presence of perchloric acid in order to prevent loss of bismuth by volatilisation of the bromide. In the case of aluminium, which is only likely to be present, if at all, in traces, a larger sample will be necessary, and it is best to use a separate portion for the determination of this element.

While it is possible to make a number of determinations on a single sample, as outlined above, in the case of standard tin of a purity of about 99·8%, it may be necessary to use larger samples for the analysis of tin of very high purity. In the present work, the largest sample used for the determination of a single impurity was 5 g., but there should be no difficulty in the use of larger samples if necessary. High grade chemicals should be used throughout, and corrections for reagent blanks should be applied in all determinations.

Lead

After removal of the tin, lead is best determined by extraction with dithizone. Of several procedures investigated, that described by Milner and Townend[2] has been found most satisfactory. In this method, the lead is extracted from a strongly ammoniacal cyanide-citrate solution, as suggested by Snyder[3]. Excess dithizone passes into the aqueous layer, and the absorption of the lead dithizonate in the organic solvent gives a direct measure of the lead content. Provided a chloroform solution of dithizone is used, 95% of the lead can be obtained in one extraction, which is not the case with a carbon tetrachloride solution. Maximum absorption of the lead dithizonate occurs at 510 mμ; the colour is stable for at least 2 hours. Under the conditions used, there is very slight interference from bismuth. According to Milner's data, 100 parts of bismuth are approximately equivalent to 3 parts of lead, and we have confirmed this. Since bismuth is in any case partially volatilised during the hydrobromic acid treatment, the interference may be considered negligible.

Reagents

(1) *Ammoniacal Cyanide Solution:* Dissolve 5 g. potassium cyanide and 1 g. sodium sulphite in 400 ml. water, and add 250 ml. concentrated ammonia solution.

(2) *Dithizone Solution:* 0·006%. Dissolve 30 mg. dithizone in 25 ml. chloroform and extract twice in a large separating funnel with 100 ml. portions of 2% ammonia. Discard the chloroform layer and wash the combined aqueous layers with about 20 ml. chloroform. Again discard the chloroform layer. Make the aqueous solution just acid by addition of concentrated hydrochloric acid and shake with 250 ml. chloroform. Separate the chloroform layer, add a further 250 ml. and shake again. Separate and combine the two chloroform extracts. Wash with water and store in a dark bottle.

Method

To a 0·5 g. sample of tin, add 10 ml. hydrobromic-acid/bromine mixture* and evaporate to dryness. Add

* 100 ml. solvent mixture contain 90 ml. hydrobromic acid and 10 ml. bromine. The object of the bromine is to oxidise the tin to the stannic form in which it is readily volatilised: it is, therefore, immaterial whether or not the second addition of hydrobromic acid contains bromine.

another 5 ml. and evaporate a second time. To the residue, add 5 ml. 1 : 1 nitric acid and boil out bromine. Cool and dilute to 100 ml. in a graduated flask. Pipette a 10 ml. aliquot into a small beaker, add 1 ml. 10% hydroxylamine hydrochloride solution and heat just to boiling. Cool, add 2 ml. 20% sodium tartrate solution and 1 drop of thymol blue indicator and neutralise with ammonia to the blue colour. Transfer to a 200 ml. separating funnel, add 65 ml. ammoniacal cyanide solution and 20 ml. dithizone solution and shake for 1 minute. Insert a roll of filter paper (Whatman 41) in the stem of the funnel and run off the chloroform layer into a small stoppered bottle. Measure at 510 mμ (Ilford 604 filters). Carry out a blank determination on the reagents and record the difference.

In the absence of iron, the reduction with hydroxylamine may be omitted. The method as described is suitable for lead contents in the range 0·01–0·20%. For larger or smaller lead contents, the size of the sample or aliquot may be varied. For very low lead contents, it may be necessary to use a larger sample weight and employ the whole of the solution. In this case it is advisable to evaporate off most of the nitric acid before reducing with hydroxylamine. With a 1 g. sample, lead contents down to 0·0005% may be determined.

Calibration

Weigh exactly 40·0 mg. lead nitrate and dissolve in a little 5% nitric acid. Dilute to 250 ml. in a graduated flask. 1 ml. = 0·10 mg. lead. From this, prepare a second solution containing 1 ml. = 0·01 mg. lead. Measure varying amounts of the standard solution (up to 0·10 mg. for the 1 cm. cell) dilute to 10 ml., add hydroxylamine hydrochloride and sodium tartrate and continue as in the above method.

Results

Sample	Lead Present %	Lead Found %
N.B.S. 431	0·19	0·22
N.B.S. 432	0·094	0·12
N.B.S. 433	0·055	0·056
N.B.S. 434	0·022	0·025
N.B.S. 435	0·015	0·015

Copper

For copper contents down to 0·01%, the hydrobromic acid method[4] can be used with a 1 g. sample of tin (see table). For lower percentages, a more sensitive method is required, and the reaction with sodium diethyldithiocarbamate was investigated. Although the sensitivity was adequate, the method was found to be insufficiently specific. In particular, lead, cadmium, bismuth, nickel and cobalt all give precipitates with the reagent in aqueous ammoniacal citrate solution. The effects of lead and cadmium can be overcome by extraction with carbon tetrachloride, in which the complexes are soluble to give colourless solutions, but the other metals still interfere. In addition, somewhat less precise results were obtained after extraction with an organic solvent. Using rubeanic acid and the procedure of Center and MacIntosh,[5] results were at first somewhat erratic, and, with solutions of higher copper content, the greenish colloidal solution precipitated out after 5–10 minutes. Addition of gum arabic was found not only to stabilise the solution and improve the reproducibility, but also to increase the sensitivity by about 25%. With this modification, the relative sensitivities of the three methods investigated were approximately as follows: hydrobromic acid 1, rubeanic acid 5, sodium diethyldithiocarbamate 9 (the comparison is made at the optimum wave-lengths for non-interference of other ions, i.e. 600 mμ, 650 mμ, and 430 mμ). Using rubeanic acid, there is an appreciable increase in colour during the first 5–10 minutes and then a very slow increase during several hours. Consequently, the procedure was standardised by making measurements after 10–30 minutes. Lead, cadmium, bismuth, iron, nickel and zinc, in amounts up to ten times the copper, were found not to interfere.

Reagents

(1) *Buffer Solution :* 400 g. ammonium acetate, 400 ml. glacial acetic acid and 200 ml. water.

(2) *Rubeanic Acid :* 0·1% solution in alcohol (stable 2 months according to Center and MacIntosh).

Method

Dissolve a 1 g. sample in 10 ml. hydrobromic-acid/bromine mixture and evaporate to dryness. Add another 5 ml. hydrobromic-acid and evaporate again. Take up with 5 ml. 1 : 1 nitric acid and boil. Neutralise with ammonia (litmus paper) and make just acid with acetic acid. Add 2·5 ml. buffer solution and 5 ml. 0·5% gum arabic solution. Transfer to a 50 ml. graduated flask and dilute to about 45 ml. Add 1 ml. rubeanic acid and dilute to volume. Measure at 650 mμ (Ilford 608 filters) in a 4 cm. cell after allowing to stand for 10 minutes.

This procedure is suitable for copper contents in the range 0·002–0·02%. For amounts less than 0·002%, a larger sample must be used. Contents up to 0·04% can be measured in a 2 cm. cell, or a smaller weight can be used. The hydrobromic acid method is preferred for the higher range, however.

Results

Sample	Copper Present %	Copper Found %	
		Hydrobromic Acid Method	Rubeanic Acid Method
N.B.S. 431	0·19	0·20	—
N.B.S. 432	0·097	0·10	—
N.B.S. 433	0·055	0·054	0·052
N.B.S. 434	0·019	0·021	0·019
N.B.S. 435	0·0077	—	0·0075

Bismuth

Although not as sensitive as the dithizone or iodide methods, the bismuth-thiourea reaction is far more specific, and a procedure based on this reaction has been described by the A.S.T.M.[6] Antimony gives a yellow colour with thiourea, but it can be removed together with tin by treatment with hydrobromic acid. Perchloric acid is added during the evaporation with hydrobromic acid to prevent volatilisation of bismuth. Lead and copper have been reported as forming colourless complexes with thiourea, and before applying the method to metallic samples the absorption curves for bismuth, lead and copper were investigated. The bismuth-thiourea colour has a maximum at 465 mμ, while lead and copper, although absorbing in the extreme violet end of the spectrum, show no absorption above 420 mμ. The bismuth colour is affected by the concentration of thiourea but the curves pass through a common point at 440 mμ. This confirms a statement by the A.S.T.M. that it is only at this wave length that the colour is independent

of the concentration of the reagent; they therefore recommend measurement at this wave length. For small amounts of bismuth it is, however, desirable to measure at the most sensitive wave length, and at 465 mμ the sensitivity is exactly double that at 440 mμ. For pure tin, there is in fact no objection to using the longer wave length, provided the addition of thiourea solution is measured accurately. In the case of alloys containing lead or copper, the thiourea partially reacts with these metals and the amount available to react with the bismuth may be altered, thus causing a low result. However, provided a fairly large excess of thiourea is used, quite large amounts of the alloying metals may be present without having an appreciable effect on the measured bismuth content. In the table, samples No. 6 and 7 show that bismuth may be accurately determined in samples containing up to 4% each of lead and copper without removal of these metals. No interference was found with 10 times the amount of cadmium, iron, nickel and zinc. If a filter photometer is used, Ilford 602 filter gives a close approximation to 465 mμ. The colour is stable for several hours.

Method

Dissolve a 2 g. sample in 20 ml. hydrobromic-acid/bromine mixture and add 5 ml. 60% perchloric acid. Evaporate until hydrogen bromide is expelled and, if the perchloric acid is cloudy, add a further quantity of hydrobromic acid. Repeat until the perchloric acid is clear, indicating complete removal of tin and antimony. Cool, dilute and transfer to a 50-ml. graduated flask. Add from a pipette 25 ml. thiourea solution (8% freshly prepared) and dilute to volume. Measure the absorption at 465 mμ. Carry out a blank on the reagents and record the difference.

Using a 4-cm. cell, this method is suitable for bismuth contents in the range 0·001–0·015%. For contents up to 0·07%, use a 1-cm. cell

Calibration

Dissolve 0·250 g. bismuth in a little nitric acid and dilute to 250 ml. 1 ml. = 1·0 mg. bismuth. Prepare a second solution containing 1 ml. = 0·1 mg. bismuth. To varying amounts of bismuth solution add 5 ml. perchloric acid and fume. Transfer to 50-ml. graduated flasks and develop the colour as described. To calibrate at 465 mμ (or with Ilford 602 filter), use amounts of bismuth up to 0·3 mg. with the 4-cm. cell, and up to 1·4 mg. with the 1-cm. cell.

Results

Sample	Sample Weights	Bismuth Present %	Bismuth Found %
N.B.S. 431	1 g.	0·020	0·021
N.B.S. 432	2 g.	0·0098	0·010
N.B.S. 433	2 g.	0·0052	0·005
N.B.S. 434	2 g.	0·0020	0·002
N.B.S. 435	5 g.	0·0011	0·001
N.B.S. 51C (7Sb, 4 Cu, 2 Pb)	1 g.	0·028	0·026
B.C.S. 178 (7Sb, 4 Cu, 4 Pb)	2 g.	0·005	0·004

Iron

Both the thiocyanate and the *o*-phenanthroline methods were investigated, but the latter was finally selected owing to its greater sensitivity and freedom from interference. The method described is similar to that given by the A.S.T.M.[6], with the exception that separation of copper by boiling with lead foil is omitted. Under the conditions described, up to about 5 mg. of copper can be tolerated. With 4 mg., or less, a pale green colour is formed which shows negligible absorption at the wave length used (510 mμ). With 5 mg., a dark blue precipitate is first formed, but, on standing for a few minutes, it redissolves to give the pale green solution. Larger amounts of copper give precipitates which are difficult to redissolve. A few other metals such as zinc and cadmium react with the reagent, and while they do not give a positive error, they decrease the amount of reagent available for reaction with the iron. This may lead to low results, unless a fair excess of *o*-phenanthroline is used. Lead does not interfere.

Reagents

(1) *Buffer Solution:* Dissolve 270 g. sodium acetate (anhyd.) in 500 ml. water, add 240 ml. acetic acid and dilute to 1 litre.

(2) *o-Phenanthroline Solution:* Dissolve 0·25 g. *o*-phenanthroline in 100 ml. hot water and allow to cool.

Method

Dissolve 1 g. sample in 10 ml. hydrobromic-acid/bromine mixture and remove tin in the usual way. Take up with 5 ml. 1 : 1 nitric acid and boil out bromine. Neutralise with ammonia and make just acid with acetic acid. Add 2 ml. 10% hydroxylamine hydrochloride solution and 15 ml. buffer solution and heat to incipient boiling to ensure reduction of iron. Cool, transfer to a 50-ml. graduated flask, add 10 ml. *o*-phenanthroline and dilute to the mark. Measure at 510 mμ (Ilford 604 filter). Carry out a blank on the reagents and record the difference. Use a 1-cm. cell for iron contents in the range 0·005–0·03% and a 4-cm. cell for contents down to 0·001%.

Calibration

Dissolve 0·100 g. pure iron wire in a little *aqua regia* and dilute to 100 ml. 1 ml. = 1·0 mg. iron. From this prepare a more dilute solution containing 1 ml. = 0·05 mg. iron.

Measure varying amounts of standard iron solution (up to 0·3 mg. iron) into small beakers, add 2 ml. 10% hydroxylamine hydrochloride solution and 15 ml. buffer solution. Heat to reduce the iron, cool, add *o*-phenanthroline, etc., as above.

Results

Since no suitable tin standards containing iron were available, some synthetic standards were prepared by adding known amounts of iron to solutions of 1 g. samples of Chempur tin, to which other metals were added in amounts likely to be present in commercial tin.

Sample	Iron Added %	Other Additions %	Iron Found
Chempur Tin	0·005	0·1 Pb, 0·1 Cu, 0·01 Bi, 0·01 Zn.	0·005
Chempur Tin	0·010	0·2 Pb, 0·1 Cu, 0·05 Bi, 0·02 Cd, 0·01 Ni.	0·011

Nickel

Nickel is determined by means of the red colour produced on adding dimethyglyoxime to an ammoniacal solution in the presence of an oxidising agent such as bromine or iodine. Since the colour is formed in

ammoniacal solution, citrate or tartrate is usually added to prevent precipitation of such metals as iron and aluminium. A spectrophotometric study of the colour reaction, using bromine water as the oxidising agent, has been made by Mitchell and Mellon,[7] who did not, however, include citrate or tartrate in the solutions investigated. They found a maximum at 445 mμ with a secondary peak at 530–540 mμ and the stability of the solution was investigated up to 68 minutes. It was found that the absorption curve undergoes a complicated change on standing, showing higher density at some wave-lengths and lower at others. The change is already apparent after 10 minutes, and after 68 minutes the density at 445 mμ has decreased by about 10% while the density at 540 mμ has increased by 20%. Isobestic points were reported at 455 mμ and 416 mμ.

In the present investigation, a similar study of the absorption curve was made, using a solution containing citrate (1 g. citric acid) and iodine as the oxidising agent. The maximum occurred at the same wave-length as reported by Mitchell and Mellon (445 mμ), but under our conditions the absorption curve was more stable, and no change occurred during the first 30 minutes. After 1 hour, the density at 445 mμ had decreased by 1% and the density at 540 mμ had increased by the same amount. Thereafter, the shape of the curve changed in much the same way as that studied by Mitchell and Mellon, giving isobestic points at 400 mμ and 460 mμ during the first 3 hours, but slowly fading at both points after 20 hours.

Using conditions essentially similar to the above (iodine and ammonium citrate) for determination of nickel in steel, Cooper[8] reported that the nickel solution is stable for at least 25 minutes at 540 mμ. When iron is present in large amounts, as in steels, it is necessary to measure at some wave-length above 500 mμ, since iron in ammoniacal citrate absorbs fairly strongly at shorter wave-lengths. When iron is present in trace amounts, however, the effect is negligible at 445 mμ. In the presence of citrate, 10 mg. of iron show an absorption equivalent to 0·03 mg. nickel at this wave-length, and, since large amounts of iron are never present in tin, it is quite safe to make use of the increased sensitivity obtained by measuring at the absorption maximum. Copper shows an absorption curve which absorbs fairly strongly at both the violet and the red ends of the spectrum, with a minimum between 440 mμ and 520 mμ. At 445 mμ, 10 mg. copper show exactly the same absorption as 10 mg. iron. A potentially more serious effect of copper is that it has been reported to cause fading of the nickel colour. This has been studied by Cooper at 540 mμ, and he found that addition of copper caused at first a slight increase in density, but that after 10 minutes fading occurred, and the rate of fading was proportional to the copper content. To find whether this effect also occurs at 445 mμ, some mixtures of nickel and copper were prepared, the colours developed with dimethylglyoxime and measured at intervals. The following results were obtained.

Nickel Added	Copper Added	Cu : Ni Ratio	Optical Density (445 mμ 1 cm. cell)					Nickel Recorded
			5 min.	15 min.	30 min.	45 min.	60 min.	
0·10 mg.	0·5 mg.	5/1	0·50	0·50	0·49	0·48	0·45	0·10 mg.
0·10 mg.	1·0 mg.	10/1	0·50	0·50	0·49	0·46	0·41	0·10 mg.
0·10 mg.	1·5 mg.	15/1	0·54	0·54	0·53	0·49	0·38	0·11 mg.
0·05 mg.	1·0 mg.	20/1	0·27	0·27	0·27	0·23	0·13	0·055 mg.
0·025 mg.	1·0 mg.	40/1	0·16	0·16	0·15	0·11	0·06	0·032 mg.

It will be seen that an effect similar to that found by Cooper does indeed occur, but the rate of fading is much slower, and is in fact negligible if the readings are made within 30 minutes. The last column of the table gives the amount of nickel corresponding to the readings obtained during the first 30 minutes. Up to 10 times the amount of copper may be present without affecting the nickel result; with higher copper-nickel ratios positive errors occur, and it may be necessary to remove the copper before determining nickel.

Reagents

(1) 50% *Citric Acid Solution:* Dissolve 500 g. citric acid in water and make up to 1 litre.

(2) *Dimethylglyoxime Solution:* Dissolve 1 g. dimethylglyoxime in 1 litre 1 : 1 ammonia solution.

Method

Dissolve a 1 g. sample in 10 ml. hydrobromic acid bromine mixture and evaporate to dryness. Add another 5 ml. hydrobromic acid and evaporate again. Take up with 5 ml. 1 : 1 nitric acid and boil out bromine. Add 2 ml. citric acid solution, neutralise with ammonia and make just acid with acetic acid. Transfer the solution to a 50 ml. graduated flask, add 1 ml. 0·1N iodine solution and 10 ml. dimethylglyoxime solution. Dilute to volume and measure the density within 5–30 minutes at 445 mμ (Ilford 601 filter). Carry out a blank on the reagents and record the difference. Use a 1 cm. cell for nickel contents in the range 0·002–0·02%, or a 4 cm. cell for contents down to 0·0005%.

Calibration

Weigh out 0·100 g. pure nickel, dissolve in a little *aqua regia* and dilute to 500 ml. in a graduated flask. Pipette 5 ml. into a 100 ml. graduated flask and dilute to volume. 1 ml. = 0·01 mg. nickel. Measure varying amounts of standard nickel solution (up to 0·20 mg. for the 1 cm. cell, and up to 0·05 mg. for the 4 cm. cell) into a series of 50 ml. graduated flasks, add 2 ml. citric acid solution, neutralise with ammonia and make just acid with acetic acid. Develop the colours with iodine and dimethylglyoxime as already described and measure at 445 mμ.

Results

Sample	Sample Weight	Nickel Present %	Nickel Found %
N.B.S. 431	0·25 g.	0·038	0·038
N.B.S. 432	0·5 g.	0·020	0·020
N.B.S. 433	1·0 g.	0·0095	0·010
N.B.S. 434	1·0 g.	0·0044	0·0045
N.B.S. 435	1·0 g.	0·0024	0·0033

Each sample contained approximately five times as much copper as nickel.

Cobalt

The most sensitive colour reaction for cobalt is with nitroso-R-salt, which gives a red colour in slightly acid solution. Other metals also form coloured complexes, but these are decomposed by boiling with nitric acid, whereas the cobalt complex is stable. Haywood and Wood[9] applied the method to the determination of cobalt in steel, and their procedure may be applied with little modification to a nitric acid solution of the residue obtained after treatment of a tin sample with hydrobromic acid. It has been claimed that small amounts of copper prevent full development of the red cobalt

complex (Young, Pinkney and Dick[10]), but, according to Stross[11], there is no interference provided sufficient reagent is added to complex both elements, the copper complex being subsequently decomposed. With conditions as in the following procedure, Stross reports no interference with 0·025 mg. cobalt and 4·0 mg. copper. With larger amounts of cobalt, relatively less copper could be tolerated; with 0·2 mg. (the highest amount that can conveniently be determined), up to 1·5 mg. copper could be present. Nitroso-R-salt itself has a yellow colour, and absorbs strongly below 460 mμ. The red colour of the cobalt complex is due to increased absorption in the region of 500 mμ, but there is no definite maximum, and measurement of the colour may be made at any wave-length between 470 and 520 mμ.

Reagents

(1) *Nitroso-R-Salt:* 0·2% aqueous solution.
(2) *Sodium Acetate Solution:* Dissolve 30 g. anhydrous salt in water and dilute to 100 ml.

Method

Dissolve a 1 g. sample in 10 ml. hydrobromic acid/bromine mixture and evaporate to dryness. Add another 5 ml. hydrobromic acid and evaporate again. Take up with 5 ml. 1 : 1 nitric acid and boil for a few minutes. Add about 5 ml. water and neutralise with 1 : 1 ammonia solution (litmus paper). Acidify with 20% v/v sulphuric acid and add 1 ml. excess. Add 5 ml. nitroso-R-salt from a pipette, followed by 5 ml. sodium acetate solution. Heat to boiling, add 2·5 ml. nitric acid and continue to boil for 1–2 minutes. Cool immediately and dilute to 50 ml. in a graduated flask. Carry out a blank on the reagents and measure the absorption of the two solutions at 500 mμ (or with Ilford 603 filters—maximum transmission 490 mμ). Record the difference.

Using a 1-cm. cell, the range is 0·002–0·02% cobalt, while with the 4-cm. cell, amounts down to 0·0005% can be determined. For larger amounts use a smaller sample.

Calibration

Weigh out 0·100 g. pure cobalt and dissolve in a little nitric acid. Dilute to 100 ml. in a graduated flask. Pipette 5 ml. into a second 100-ml. flask and dilute to volume. 1 ml. = 0·05 mg. cobalt. For calibration of the 4-cm. cell, prepare a more dilute solution containing 1 ml. = 0·01 mg. cobalt. Measure varying amounts of standard solution (up to 0·2 mg. for 1-cm. cell), add 1 ml. 20% sulphuric acid 5 ml. nitroso-R-salt, etc. Carry out a blank on the reagents and record the differences.

Sample	Cobalt Present %	Cobalt Found %
N.B.S. 431	0·021	0·024
N.B.S. 432	0·011	0·012
N.B.S. 433	0·0045	0·0051
N.B.S. 434	0·0020	0·0021
N.B.S. 435	0·0011	0·0010

Each sample contained approximately ten times as much copper as cobalt.

Aluminium

Aluminium may be determined by extraction with a chloroform solution of oxine from a slightly alkaline solution. Several metals interfere and must either be removed or be complexed. Gentry and Sherrington[12] describe a method in which aluminium can be determined in the presence of iron, copper, nickel, cobalt and zinc, after complexing with cyanide and reducing iron with sodium sulphide. Lead, if present, is precipitated as the sulphide, and, although small amounts do no harm, it is better to remove it at an earlier stage. According to Gentry and Sherrington, tartrate interferes, but other workers (Kassner and Ozier[13] and Kenyon and Bewick[14]), have used the method successfully in the presence of small amounts of tartrate, and its use would appear to be desirable to prevent precipitation of aluminium hydroxide. The aluminium oxinate forms a pale yellow solution with an absorption maximum at 390 mμ. With a Spekker absorptiometer, measurement may be made with a mercury lamp and Chance OV1 plus Wratten 2 filters to isolate the 405 mμ line.

Reagents

(1) *Sodium Cyanide Solution:* 10%.
(2) *Oxine Solution:* 1% in chloroform. The solution should be colourless.

Method

Dissolve 1 g. sample in hydrobromic acid/bromine mixture and evaporate to dryness. Add another 5 ml. and evaporate again. Take up with 5 ml. 1 : 1 nitric acid and boil out bromine. Evaporate to dryness and take up with 20 ml. 10% perchloric acid. Add 1 ml. 20% sodium tartrate solution and pass hydrogen sulphide for 5–10 minutes. Filter off any precipitate (Whatman 540), and add 10 ml. sodium cyanide solution. Add 1 drop of thymol blue indicator and adjust with 1 : 1 nitric acid or 1 : 1 ammonia solution to the blue colour (*p*H 9·6). Transfer to a separating funnel and dilute to 50 ml. Add 25 ml. oxine solution and shake for 3 minutes. Allow to separate and run off the chloroform layer, through a roll of filter paper inserted in the stem of the funnel, into a small stoppered bottle. Measure at 390 mμ. Carry out a blank on the reagents and record the difference.

With a 1-cm. cell, the range is approx. 0·001–0·010% aluminium; with a 4-cm. cell, contents down to 0·0002% can be determined.

Calibration

Weigh out 0·125 g. pure aluminium and dissolve by heating with a little 1 : 1 nitric acid. Dilute to 500 ml. in a graduated flask. Pipette 10 ml. into a second 500-ml. flask and dilute to volume. 1 ml. = 0·005 mg. aluminium. Measure out varying amounts of aluminium solution (up to 0·1 mg.) into a series of separating funnels and to each add 20 ml. 10% perchloric acid. Add 1 ml. 20% sodium tartrate solution and 10 ml. sodium cyanide solution and adjust to the blue colour of thymol blue. Dilute to 50 ml. and extract with oxine.

Results

No tin standards containing aluminium were available, but four samples of 50/50 tin-lead solder containing small percentages of aluminium, and which had been analysed spectrographically, gave the following results.

Aluminum Found Spectrographically %	Sample Weight	Aluminium Found Photometrically %
0·005	1·5 g.	0·0039
0·01	0·5 g.	0·010
0·02	0·5 g.	0·018
0·04	0·25 g.	0·040

Zinc

Traces of zinc may be determined with dithizone according to the method of Butts, Gahler and Mellon[15]. The extraction is made from a nearly neutral solution containing cyanide and bis (2-hydroxyethyl) dithiocarbamate, which prevent interference from moderate amounts of copper, lead, cadmium and nickel. This is an improvement on the method of Cowling and Miller[16], using sodium diethyldithiocarbamate as the complexing agent, since only small amounts of cadmium (half that of the zinc) may be tolerated in this method. Bis (2-hydroxyethyl) dithiocarbamate has also been used to complex nickel during the determination of zinc in nickel plating baths (Serfass, Levine, Prang and Perry [17]). Unlike lead and cadmium, zinc cannot be extracted by one treatment with dithizone, and repeated extractions are necessary. The excess of dithizone remains in the organic solvent layer, and must subsequently be removed by shaking with dilute sodium sulphide solution. A carbon tetrachloride solution of dithizone is used, since it is easier to separate the excess dithizone from this solvent than from chloroform. Zinc dithizonate shows an absorption maximum at 535 mμ.

Reagents

(1) *Bis (2-Hydroxyethyl) Dithiocarbamate:* Dissolve 4·0 g. diethanolamine and 1 ml. carbon disulphide in 40 ml. methyl alcohol. The solution will keep for 3–4 days

(2) *Dithizone Solution:* 0·005%. Dissolve 25 mg. dithizone in 250 ml. carbon tetrachloride. Shake with 200 ml. 2% ammonia solution in a large separating funnel and discard the carbon tetrachloride layer. Make the aqueous solution just acid by addition of concentrated hydrochloric acid and shake with 250 ml. carbon tetrachloride. Separate the carbon tetrachloride layer, add a further 250 ml. and shake again. Separate and combine the carbon tetrachloride extracts. Wash with water and store in a dark bottle.

Method

Dissolve a 1 g. sample in 10 ml. hydrobromic-acid/bromine mixture and evaporate to dryness. Add another 5 ml. hydrobromic acid and evaporate again. Take up with 5 ml. 1 : 1 nitric acid and boil. Cool and dilute to 100 ml. in a graduated flask. Pipette a 25 ml. aliquot into a separating funnel, add one drop of methyl red, 2 ml. 20% sodium tartrate solution and then ammonia solution until yellow. Add 1 ml. 5% sodium cyanide solution and then 1 : 1 acetic acid, dropwise, to a neutral peach colour. Extract the methyl red by shaking with 5 ml. carbon tetrachloride and discard. Add 1 ml. bis (2-hydroxyethyl) dithiocarbamate and extract the zinc with dithizone as follows. Shake for 1 minute with a 10 ml. portion, allow to separate and run the carbon tetrachloride layer into another separating funnel. Then shake with 5 ml. portions of dithizone, running each successive extract into the second separating funnel until there is no change in the colour of the dithizone solution. Wash finally with a few ml. of carbon tetrachloride and add to the combined extracts. Discard the aqueous solution in the first separating funnel. Remove the excess dithizone from the carbon tetrachloride solution by shaking first with 20 ml. and then with 10 ml. portions of 0·04% sodium sulphide solution, until the upper layer of sodium sulphide solution is colourless. Run the red carbon tetrachloride solution into a dry 50 ml. graduated flask and make up to the mark with carbon tetrachloride. Carry out a blank on the reagents and measure the colour intensities of the two solutions at 535 mμ (Ilford 604 filters). A 1-cm. cell gives a range of 0·004–0·015% zinc, and with a 4-cm. cell down to 0·0005% can be measured. For larger or smaller amounts, different aliquots or sample weights must be used. The amount of copper or lead in the aliquot taken should not exceed 2 mg.

High grade reagents must be used to avoid high blanks. At one stage during the investigation of this method, very high blanks were encountered, and were found to be due to a supply of A.R. ammonia solution which contained 5 p.p.m. zinc. A "Laboratory Reagent" grade of ammonia from another supplier was found to be free from zinc.

Calibration

Dissolve 0·100 g. pure zinc in dilute hydrochloric acid and make up to 1 litre. 1 ml. = 0·1 mg. zinc. From this, prepare two further solutions containing, respectively, 0·005 and 0·001 mg. per ml. To calibrate with the 1-cm. cell, measure varying amounts up to 0·004 mg. zinc into separating funnels and dilute to 25 ml. Add methyl red, sodium tartrate, etc., and extract as above. With the 4-cm. cell, use from 0·002 to 0·010 mg. zinc.

Number of Extractions Necessary

The amounts of dithizone used in one series of experiments to extract varying amounts of zinc are shown below.

mg. Zinc.	ml. Dithizone
0·01	10 + (2 × 5)
0·02	10 + (3 × 5)
0·03	10 + (6 × 5)
0·04	10 + (7 × 5)

If the amount of zinc is known to be 0·03–0·04 mg., an initial extraction may be made with 25 ml. of dithizone. If an unknown is found to require more than 45 ml., then a smaller sample must be used.

Sample	Sample Weight*	Zinc Present %	Zinc Found %
N.B.S. 431	0·07 g.	0·041	0·051
N.B.S. 432	0·1 g.	0·020	0·023
N.B.S. 433	0·2 g.	0·0095	0·0092
N.B.S. 434	0·3 g.	0·0046	0·0039
N.B.S. 435	0·35 g.	0·0020	0·0024

* This refers to the weight of sample in the aliquot and not the amount weighed out.

Cadmium

Traces of cadmium may be determined by extraction with dithizone from a basic solution. Several metals interfere, and these may be conveniently removed by the procedure described by Butts, Gahler and Mellon[15]. Copper and iron are removed by extraction of the cupferrides with chloroform, and after destroying any remaining trace of cupferron with bromine water, the cadmium is precipitated as the brucine-cadmium-iodide complex. Extraction of this complex into chloroform effects a separation from nickel and zinc. The cadmium is removed from the chloroform with dilute hydrochloric acid, and the final extraction of cadmium with dithizone carried out after making alkaline with sodium hydroxide. Excess dithizone passes into the aqueous layer, leaving the red cadmium dithizonate in the organic solvent. About 95% of the cadmium is extracted by one treatment with dithizone. Maximum absorption occurs at 510 mμ.

In this procedure, any lead accompanies the cadmium during the brucine separation and is present during the final extraction. However, lead is not extracted from

strong sodium hydroxide solution, provided a carbon tetrachloride solution of dithizone is used; with a chloroform solution, there is a slight error when a large excess of lead is present.

REAGENTS

(1) *Cupferron Solution*: 1% aqueous solution, freshly prepared.

(2) *Potassium Iodide Solution*: 10%.

(3) *Brucine Sulphate Solution*: Dissolve 2 g. brucine sulphate by warming with 100 ml. 5% acetic acid.

(4) *Dithizone Solution*: 0·005%. Prepare as described in the determination ot zinc.

METHOD

To a 0·5 g. sample of tin add 10 ml. hydrobromic acid/bromine mixture and evaporate to dryness. Add another 5 ml. and evaporate a second time. To the residue, add 5 ml. 1 : 1 nitric acid and boil for a few minutes. Cool, add 5 ml. 20% sodium tartrate solution and one drop of methyl red and make just alkaline with 20% sodium hydroxide solution. Acidify with 2 ml. acetic acid and transfer to a 100 ml. separating funnel. Add 5 ml. cupferron solution and shake with 10 ml. chloroform. Allow to separate and discard the chloroform layer. Repeat with another 10 ml. chloroform. To the aqueous solution remaining in the funnel, add 1 ml. bromine water and, after standing for 1 minute, extract the excess bromine by shaking with two 5 ml. portions of chloroform. Add 1 ml. 10% hydroxylamine hydrochloride solution. Then add 5 ml. potassium iodide solution and 5 ml. brucine sulphate solution. Extract three times with 15 ml. portions of chloroform and collect the chloroform extracts in a second separating funnel (200 ml.). Discard the aqueous layer in the first funnel. Shake the extracts in the second funnel with 20 ml. 5% hydrochloric acid. Run off the chloroform layer into another funnel and shake with a further 10 ml. 5% hydrochloric acid. Discard the chloroform layer and combine the two hydrochloric acid extracts. Add 30 ml. 20% sodium hydroxide solution and 20 ml. dithizone solution and shake 1 minute. Insert a roll of filter paper (Whatman 41) into the stem of the funnel and run off the carbon tetrachloride layer into a small stoppered bottle. Measure at 510 mμ (Ilford 604 filter). Carry out a blank determination on the reagents and deduct.

The method as described is suitable for cadmium contents in the range 0·0002–0·006%. For larger contents use a smaller sample.

CALIBRATION

Weigh out 0·250 g. pure cadmium, dissolve in a little dilute nitric acid and make up to 500 ml. in a graduated flask. 1 ml. = 0·5mg. cadmium. From this, prepare a second solution containing 1 ml. = 0·005 mg. cadmium. Measure varying amounts of standard solution (up to 0·03 mg. for the 1 cm. cell) into a series of separating funnels, dilute to 30 ml. add 30 ml. 20% sodium hydroxide and extract with dithizone as described.

RESULTS

Sample	Sample Weight	Cadmium Present %	Cadmium Found %
N.B.S. 431	0·1 g.	0·020	0·020
N.B.S. 432	0·2 g.	0·0095	0·010
N.B.S. 433	0·4 g.	0·0053	0·0042
N.B.S. 434	0·8 g.	0·0020	0·0017
N.B.S. 435	1·0 g.	0·0011	0·0010

Sulphur

When tin is dissolved in concentrated hydrochloric or hydrobromic acid, the sulphur is evolved as hydrogen sulphide, and this may be absorbed in zinc acetate solution and determined volumetrically in the usual way. The volumetric method has the disadvantage that very large sample weights of tin are required. The sulphur content of tin never exceeds 0·01%, and at least 25 g. of finely divided sample are required; more usually it is necessary to use 50 or 100 g. If the absorbed hydrogen sulphide is determined by the photometric methylene blue method, much smaller samples can be taken. Using the procedure of Budd and Bewick,[18] it was found that sulphur contents down to 0·0001% may be determined with a 2 g. sample.

Attempts were at first made to use hydrobromic acid as the solvent, since tin will dissolve much more rapidly in this than in hydrochloric acid, but it was found that even the purest hydrobromic acid contained traces of sulphur compounds which were reduced to H_2S on boiling with stannous salts. Re-distillation of the hydrobromic acid reduced the amount of sulphur compounds, but they could not be entirely eliminated, even by several distillations. This reduction does not occur if hydrochloric acid is used, possibly owing to the lower boiling point, and only the sulphide sulphur is evolved. Concentrated hydrochloric acid cannot be used to dissolve the tin since gaseous hydrogen chloride will pass into the receiving vessel, and large amounts of chloride interfere with the methylene blue method. It was found that finely divided tin will dissolve reasonably rapidly in 1 : 1 hydrochloric acid (very nearly the constant boiling composition), provided a little antimony trichloride is added. The methylene blue is formed from *p*-aminodimethylaniline (dimethyl-*p*-phenylenediamine) by the action of hydrogen sulphide and a ferric salt. The colour shows an absorption maximum at 670 mμ.

REAGENTS

(1) *Antimony Trichloride Solution*: Dissolve 2 g. antimony trichloride in 100 ml. concentrated hydrochloric acid.

(2) *Zinc Acetate Solution*: Prepare a stock solution containing 200 g. zinc acetate dihydrate per litre. Dilute 10 times before use and add a few drops of acetic acid to the dilute solution.

(3) p-*Aminodimethylaniline Solution*: Prepare a stock solution by dissolving 2·72 g. *p*-aminodimethylaniline sulphate in 7·5 ml. 1 : 1 sulphuric acid and diluting to 10 ml. with 1 : 1 sulphuric acid. This solution will keep for several months.

The solution to be used contains 1 ml. of the stock solution diluted to 40 ml. with 1 : 1 sulphuric acid. This will keep for about 1 month.

(4) *Ferric Chloride Solution*: Dissolve 100 g. of the hexahydrate in water and dilute to 100 ml.

APPARATUS

A 150 ml. flask provided with a funnel, hydrogen inlet and a delivery tube reaching to the bottom of a 50 ml. graduated flask surrounded by a beaker of cold water. The end of the delivery tube should be detachable so that it can be placed inside the graduated flask, and should be joined to the apparatus by a small piece of polythene tubing.

Method

Weigh 2 g. of tin, preferably in the form of sawings, into the 150 ml. flask, and place 35 ml. 2% zinc acetate solution into the graduated absorption flask. Pass a stream of hydrogen or nitrogen, first bubbled through 5% zinc acetate solution, through the apparatus, and after 5 minutes, add 40 ml. 1 : 1 hydrochloric acid plus three drops of antimony trichloride solution. Warm gently until the tin has dissolved (about 45 minutes) and then heat to boiling and boil for 1 minute. Disconnect the end of the delivery tube and place inside the absorption flask. Add 1·5 ml. *p*-aminodimethylaniline solution, mix and then add 5 drops of ferric chloride solution. Make up to the mark, allow to stand for 15 minutes and measure in a 1- or 4-cm. cell at 670 mμ (Ilford 608 filter). Carry out a blank determination as follows. Allow the solution in the reaction flask to cool, and in the meantime place into position another 50 ml. graduated flask containing 35 ml. 2% zinc acetate solution. Pass hydrogen, add another 40 ml. 1 : 1 hydrochloric acid after 5 minutes and heat gradually to boiling. Boil for 1 minute and continue as before. Record the difference in density and read from the graph.

Calibration

Prepare a standard sulphide solution as follows. Weigh 1·2 g. dry sodium sulphide crystals into a beaker, rinse rapidly with a little water to remove sulphite and discard the washings. Dissolve the remaining crystals in water and make up to 1 litre. Pipette 100 ml. into 250 ml. water, add 25 ml. 0·1 N iodine and 25 ml. 0·1 N hydrochloric acid (approx.). Titrate excess iodine with 0·1 N sodium thiosulphate and find the amount of iodine which has reacted with the sulphide solution. Calculate the volume of sulphide solution which will contain 1·0 mg. sulphur (1 ml. 0·1 N iodine = 0·0016 g. sulphur), measure this volume accurately with a burette and dilute to 500 ml. (Solution A, 1 ml. = 0·002 mg. sulphur). Prepare a second solution five times the strength of solution A (Solution B, 1 ml. = 0·010 mg. sulphur). Since the sulphide solutions are unstable, they should be prepared immediately before making the calibration.

To calibrate with the 4 cm. cell, measure varying amounts of Solution A (up to 0·03 mg. sulphur) into a series of 50 ml. graduated flasks and dilute to 35 ml. with 2% zinc acetate solution. Add *p*-aminodimethylaniline and ferric chloride, and measure the methylene blue colour as already described. To calibrate the 1 cm. cell, use varying amounts of Solution B, up to 0·10 mg.

Results

No standard tins containing sulphur were available. A sample of tin was analysed volumetrically using a 50 g. sample (dissolved in 150 ml. concentrated hydrochloric acid, and the absorbed hydrogen sulphide titrated with N/50 potassium iodate solution) and also photometrically using a 2 g. sample, and a result of 0·0003% was obtained in each case. All other samples of tin examined by the photometric method gave results between 0·0002% and 0·0005% sulphur.

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REFERENCES

1 Coppins & Price, *Metallurgia*, 1952, **46**, (273) 52.
2 Milner and Townend, *Anal. Chim. Acta*, 1951, **5**, 584.
3 Snyder, *Anal. Chem.*, 1947, **19**, 684.
4 Coppins and Price, *Metal Industry*, 1951, **78**, (11) 203.
5 Center and MacIntosh, *Ind. Eng. Chem.* (*Anal*), 1945, **17**, 239.
6 "Chemical Analysis of Metals," 1950.
7 Mitchell and Mellon, *Ind. Eng. Chem.* (*Anal*), 1945, **17**, 380.
8 Cooper, *Anal. Chem.*, 1951, **23**, 875.
9 Haywood and Wood, *J.S.C.I.*, 1943, **62**, 37.
10 Young, Pinkney and Dick, *Ind. Eng. Chem.* (*Anal*), 1946, **18**, 474.
11 Stross, *Metallurgia*, 1952, **45**, 315.
12 Gentry and Sherrington, *Analyst*, 1946, **71**, 432.
13 Kassner and Ouier, *Anal. Chem.*, 1951, **23**, 1453.
14 Kenyon and Bewick, *Anal. Chem.*, 1952, **24**, 1826.
15 Butts, Gabler and Mellon, *Sewage and Industrial Wastes*, 1950, 1643.
16 Cowling and Miller, *Ind. Eng. Chem.* (*Anal*), 1941, **13**, 145.
17 Serfass, Levine, Prang and Perry, *Plating*, 1949, **36**, 818.
18 Budd and Bewick, *Anal. Chem.*, 1952, **24**, 1536.

Symposium in Analytical Chemistry, 1954

Arrangements for the Symposium on Analytical Chemistry to be held in the University of Birmingham between August 25th and September 1st, 1954, are progressing, and it is now possible to make an interim announcement. There will be three or four plenary lectures, the remaining lectures being divided into two distinct categories: (1) original and unpublished work, and (2) authoritative surveys of recent advances in specialised fields of analytical chemistry and industrial analysis. These will include papers presented by a number of chemists of international repute.

There will also be an exhibition of specialised apparatus by the trade, and demonstrations of special techniques, whilst a collection of rare old chemistry books on view will include the Joseph Priestley collection. Visits of scientific and non-scientific interest will be arranged and there will be a number of social functions during the period of the symposium.

Induction Stirrer in Arc Melting

A new Swedish technique for stirring steel in arc furnaces has lately attracted considerable attention abroad. Developed by the ASEA Electric Company, of Vasteras, the method consists of replacing the manual stirring of the steel baths with electric induction stirrers. The first stirrer of this kind to be used outside Sweden, and the biggest ever built, was delivered early this year by ASEA's American subsidiary, Aros Electric Inc., to the Timken Roller Bearing Company, Canton, Ohio.

Mounted under an 80-ton, 20,000 kVA arc furnace, more than 20 ft. in diameter, the stirrer has a consumption of 485 kVA. The stirrer and the motor generator have been built by the Elliot Company in the U.S.A. in accordance with ASEA designs and patents, while certain parts of the equipment were manufactured in Sweden.

The first induction stirrer was put into operation in Sweden in 1947, and a number of units have in recent years been supplied to leading Swedish steelworks. Several stirrers are at present being built for delivery to customers outside Sweden, including a unit for a 150-ton arc furnace for a Belgian steelworks. The main characteristic of the ASEA stirrer is that the unit is placed below the bottom of the furnace, which prevents mechanical and thermal wear. In principle, the unit works as an asynchronous motor. The frequency is very low in order to ensure the necessary stirring power and to cause a minimum of thermal losses in the furnace bottom, which has to be non-magnetic and is usually made of stainless steel.